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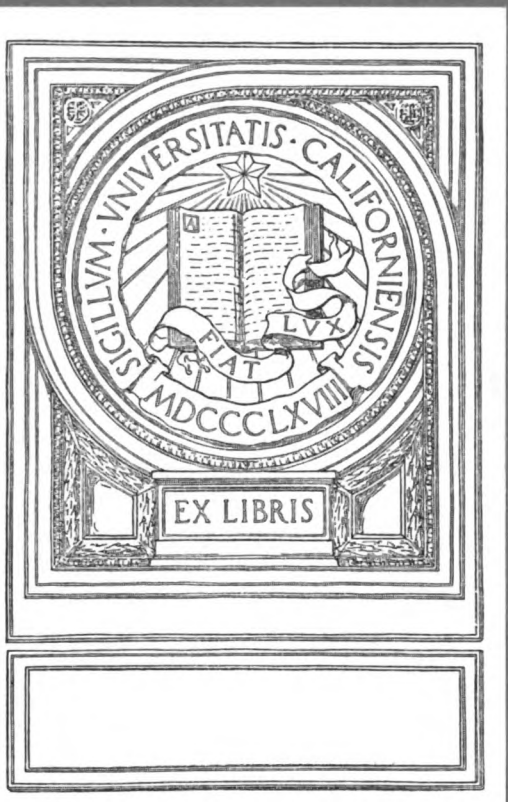

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PROCEEDINGS OF

THE ROYAL SOCIETY.

Section A.—Mathematical and Physical Sciences.

The Chemical Physics involved in the Precipitation of Free Carbon from the Alloys of the Iron-Carbon System.

By W. H. Hatfield, B. Met. (Sheffield University).

(Communicated by Prof. W. M. Hicks, F.R.S. Received October 7,—Read November 10, 1910.)

[Plates 1—5.]

As a result of recent research* it is held that the iron-carbon alloys must be considered as an iron-iron carbide system as indicated in the accompanying diagram; the author is satisfied that the double diagram based on the assumption of a metastable and a stable equilibrium is inaccurate, since, in the liquid or the solid state, that carbon which is in solution is contained in solution as carbide.

The experiments to be described afford evidence that the carbide must separate out from the solution before free carbon can appear, and that it is only the structurally free carbide that can dissociate; free carbon will not separate from the solid solution.

The influence of silicon, sulphur, and manganese upon the precipitation are investigated, with the following results:—

1. The silicon (if it be the only foreign element present) is not uniformly distributed through the material. The carbide, whilst not containing so much as the matrix, has present a percentage increasing with the silicon content of the alloy.

2. The manganese is largely found in the carbide to the exclusion of the silicon.

* Goerens, 'Metallurgie,' 1906, vol. iii; 1907, vol. iv.

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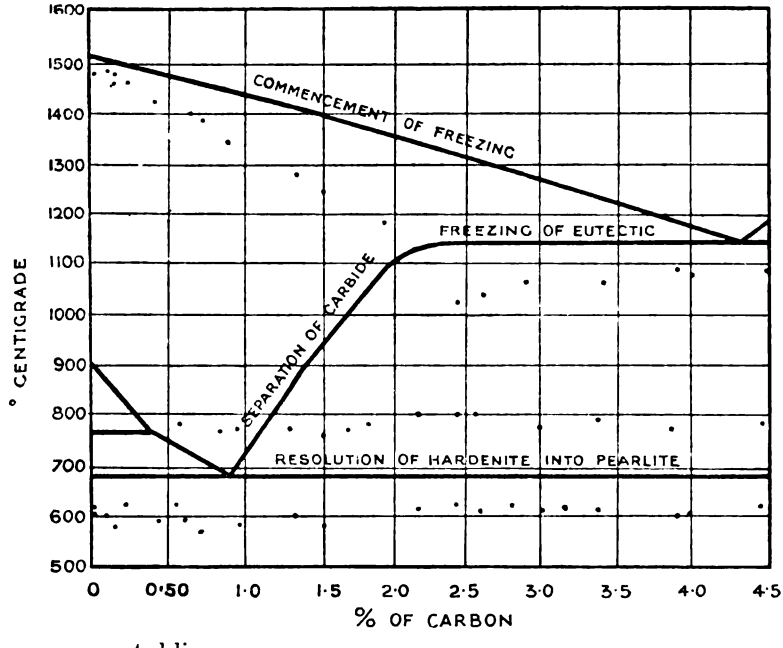
3. The sulphur appears to cause the exclusion of the silicon from the carbide, but the methods employed failed to reveal the presence of any quantity of sulphur in that constituent.



——— = accepted lines.

. . . . = readings obtained by Carpenter and Keeling which suggest other lines.

4. The heat treatment experiments indicate that the presence of these elements, by modifying the composition of the carbide, renders it more or less difficult to dissociate at a given temperate. Further, by altering the composition of the alloy, the solubility of the carbide in the austenite was modified and therefore more or less free carbide was subjected to the conditions of dissociation.

It is also shown that the space occupied by, and the structure of, the free "annealing" carbon nodules are determined by the size and structure of the free carbide from which they are produced.

The precipitation of free carbon during cementation is discussed and the phenomenon of "black" steel is considered in the light of the observations made during the research.

The Free Carbon as Found in the Iron-Carbon Alloys.

The free carbon observed in the alloys of iron and carbon is always one of the two varieties, graphite or annealing carbon.

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Graphite is formed immediately after the solidification of the eutectic, and its distinctive form is most probably due to the influence of the primary crystallization. Obviously upon an examination of the iron-carbon freezing diagram it will be seen that the graphite could not be produced previous to the freezing of the eutectic, otherwise it would not be found evenly distributed through the mass, but would have risen by its own specific gravity to the surface. Further, as the eutectic is proved to consist of 4·3 per cent. of carbon in combination, it will be necessary for the eutectic to separate into carbide and austenite, before the carbide can dissociate and thus give birth to the free carbon. At the point of solidification, the solubility of the iron for the carbon is that of the eutectic composition, 4·3 per cent., but the change from the liquid to solid state reduces the solubility to such an extent that the separation of the superfluous carbide causes the distinct evolution of heat which is known to take place at about 1137° C. In irons such as the highly siliceous ones, it is difficult to conceive* how the carbide in the finely divided state, in which it exists immediately after this separation, can live through the immediately subsequent conditions.

The following corroborative evidence should be considered: Two bars (2″ × 1″ × 12″) were cast of the following composition :—

C.....	3·20 per cent.	S.....	0·02 per cent.
Si	1·10 „	P	0·20 „
	Mn.....	0·41 per cent.	

The first, cast with the metal at about 180° C. higher temperature than the other, in fracture was mottled, and the second was perfectly grey. The unetched microstructure of the grey bar is shown in fig. 1, Plate 1, and to one accustomed to white iron structures it shows that the primary cementite has decomposed *in situ*. Fig. 2, Plate 1, shows the structure when etched, and indicates that it is only the structurally free carbide that has dissociated.

The microstructure of the mottled bar, fig. 3, Plate 1, indicates that the precipitation commences at several centres, and if continued spreads through the mass. In fig. 4, Plate 1, the unetched structures of the free carbon areas are illustrated. It will be seen that the free carbon exactly conforms in structural position with that held by the cementite. As previously shown by the author† the initial casting temperature materially influences the dissociation of the carbide.

In these instances the free carbon would unquestionably be classed as graphite, and the microstructures throw light upon the manner of the birth

* Heyn and Bauer, 'Stahl und Eisen,' vol. 27, 1565—71 and 1621—25.

† Hatfield, 'Iron and Steel Institute Journal,' 1906, vol. i.

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of graphite. Fig. 26, Plate 4, shows the typical graphitic iron, which results from prolonged cooling of these bars.

Annealing carbon differs little from graphite except in that the temperature at which it is precipitated being low the amorphous form is retained. The composition of the iron, the size and structure of the cementite or free carbide, and the temperature at which the carbide dissociates, are, as will be shown, the determining factors of the size and character of the annealing carbon. As an instance of the influence of the size of the free carbide upon the size of annealing carbon the results of the following experiment are given.

Two test bars of white cast iron of the following composition were made:—

Si	0·70 per cent.	S	0·04 per cent.
Mn.....	0·80 „	P	0·11 „
C	3·40 per cent.		

One bar A was allowed to cool normally, its microstructure is shown in fig. 5, Plate 1. The other bar B was quenched when it had cooled to 1000° C., and the structure of this one will be seen in fig. 7, Plate 1. It will be noticed that whereas in the naturally cooled bar the cementite is in large thick membranes, in the quenched one the structure is very different. The matrix seen in the micrograph of B actually contains considerably more carbon in solution than is present in the pearlite of A. In fig. 25, Plate 4, is seen the microstructure of a globule of this iron when poured molten into a mass of cold water; it illustrates the comparative structure of iron approximating to the eutectic composition shortly after solidification.

Samples A and B were heated to a temperature of 1050° C., maintained there for three-quarters of an hour, and quenched at a temperature of 1030° C. Fig. 6, Plate 1, illustrates the microstructure of the bar A, and if the structure is compared with its condition before this heat treatment it would appear that the annealing carbon results from the dissociation of the cementite membranes of carbide observed before the treatment.

The heat treated bar B presented a structure shown in fig. 8, Plate 1. The whole of the small cementite had decomposed, with the result that this bar contains no cementite, but only small annealing carbon nodules in martensitic austenite, as seen when examined under a high power.

This experiment indicates that the size of the original cementite is certainly an influence in determining the size of annealing carbon, and it might be well at this point to refer to a very interesting paper by Mr. Levy.*

* Levy, 'Journal Iron and Steel Institute,' 1908, vol. 2.

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His theory that it is necessary for the carbide to ball up before it can dissociate would appear to be disproved.

The author has made the statement that the "annealing carbon" sometimes appears to be merely dissociated carbide, *i.e.* a mixture of finely divided iron and carbon occupying the position of the original cementite. He would refer to two of his micrographs illustrating this phase, fig. 27, Plate 4. Here it will be seen that in a sample of white cast iron, which was undergoing heat treatment at the comparatively low temperature of 835° to 840° C., the cementite of a whole area of the section decomposed *in situ*. The micrograph of the drastically heat-treated blister-steel, fig. 34, Plate 5, is an example of the annealing carbon occupying a similar position and of a similar size to the original cementite. On further heat treatment such mixtures of free carbon and iron undergo a change, the carbon segregating, and the precipitated iron entering structurally into the mass. As an instance of this, fig. 11, Plate 2, represents the microstructure of a bar of heat treated white iron quenched at about 860° C. If this temperature be maintained for a considerable time after the precipitation of the annealing carbon the structure is as shown in fig. 12, Plate 2.

Influence of Varying Composition upon the Purity of the Structurally Free Carbide.

The presence of silicon, sulphur, and manganese is well known to influence the precipitation of annealing carbon, and the author therefore decided to determine the manner in which this influence was brought to bear.

Four irons of varying composition were chosen for experiment and were of the following analysis :—

	C.	Cr.	Si.	Mn.	S.	P.
A	3·62	nil	1·20	0·18	0·011	0·041
B	3·2	„	0·81	0·14	0·010	0·04
C	3·4	„	0·85	2·66	0·012	0·041
D	3·16	„	0·97	0·04	0·45	0·04

The micrographs of these four materials are shown in Plate 3, figs. 13, 14, 15, and 16, and are seen to consist as usual of cementite carbide (Fe_3C) and pearlite. From bars hardened at 740° C. quantities of the respective carbides were obtained. On analysis, they were found to be of the following composition :—

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Bar.	Si.	Mn.	C.
	per cent.	per cent.	per cent.
A	1·09	0·19	6·79
B	0·61	0·16	6·40
C	0·15	3·74	7·20
D	0·37	traces	6·60

The method, though crude, gave interesting results. It may be mentioned that the whole of the silicon, apart from that found in the carbide, was found in the solution, it having perfectly entered into solution in the cold dilute hydrochloric acid. The exposure of the material to the acid was of 48 hours' duration in each case. When the bars in the unhardened condition were decomposed in the same manner the analysis of the residues gave vastly different results, which were as follows :—

Bar.	Si.	Mn.
	per cent.	per cent.
A	2·15	0·28
B	1·01	0·19
C	1·45	3·62
D	0·49	traces

The silicon was therefore not dissolved by the HCl as in the former instances. This may be explained after careful consideration of the physical condition under which the "silicide" exists in such samples. Since, however, the pearlite exists as hardenite at the temperatures now being discussed, the problem may, for the present, be dismissed.

The author would claim the following deductions from these experiments :—

1. That the silicon is not uniformly distributed through the material, but that the carbide, whilst not containing as much silicon as the matrix, contains an appreciable quantity, corresponding to some extent to the total percentage.

2. That in the case of sample C the manganese is found largely in combination in the carbide, to the exclusion of the silicon.

3. In the case of the high sulphur iron the silicon is abnormally low in the carbide, and although the sulphur is not found in it, it would be deduced that it is responsible for the comparative absence of the silicon. The ease with which sulphur compounds are decomposed by even dilute hydrochloric acid would lead one to believe that though it is not found in the carbide it

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does not follow that some of it was not there originally. The author is aware, however, that the sulphur prints give contrary evidence.

Influence of Composition upon Precipitation of "Annealing" Carbon in White Iron.

Charpy and Grenet publish some interesting figures upon the influence of silicon on the precipitation of annealing carbon in their paper on "The Equilibrium of the Iron and Carbon System."* Irons of varying composition were poured into water, thus obtaining irons up to very high silicon content in the white state.

Although Charpy and Grenet state that the samples all had the normal white iron structure, the free carbide in their samples would be smaller and in less quantity than in a normal casting and the matrix much higher in carbon, facts which must be taken into account in comparing the two series of results. The author's micrographs, figs. 5 and 7, Plate 1, and fig. 25, Plate 4, illustrate the condition and quantity of carbide likely to have been present in these samples, representing as they do the structures of normal white iron, white iron quenched from 1000° C. and from the molten state respectively. With abnormal silicon, however, this would be the only way to entrap the carbon in the combined state.

The author's heat treatments were made in a Clinch-Jones muffle, and this ensured that the material, by being heated in a reducing atmosphere of unignited gas, was not decarburized. Bars A, B, C, and D, Plate 2, figs. 13, 14, 15, and 16, recently described, were placed in the muffle standing at 920° C., and were maintained at this temperature for one hour and then carefully quenched in iced brine.

After quenching, microsections were taken from these bars and etched. The results are to be found in Plate 3, figs. 17, 18, 19, and 20.

In each case it will be seen that the cementite is beginning to disappear. This is explained by the increasing solvent action of the matrix for carbide, owing to the rise in temperature to 920° C. In the case of A it is clear that the cementite had to an extent redissolved in the matrix, but that some of the remaining cementite had decomposed. In the case of B considerable areas of cementite have redissolved in the matrix, whilst several nodules of annealing carbon are seen. In the case of C no annealing carbon is observed, and further the cementite seems much corroded, having obviously been to a considerable extent dissolved in the matrix. In the case of D similar changes have taken place in the structure.

* 'Bulletin de la Société d'Encouragement pour l'Industrie Nationale,' vol. 10 pp. 399—407.

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In the second series samples of the same composition were maintained for one hour at 1050° C. and quenched from that temperature. Plate 3, figs. 21, 22, 23, and 24, illustrates the structures obtained. In the case of A all the cementite has disappeared. Some is in solution in the austenite and the remainder is dissociated into iron and carbon. Micrograph fig. 21 illustrates the structure. In the case of B all the cementite has disappeared. It is either in solution in the austenite or dissociated into iron and carbon. Micrograph fig. 22 illustrates this. The carbon would appear to be further segregated, but since both samples were treated alike the author is unable to explain this. This variation, however, may be traced to the form and size of the original cementite.

In the case of C the cementite is partly in solution, partly decomposed, and the annealing carbon occurs in a matrix of austenite in which the martensitic structure is well developed. Only traces of undissociated carbide remain. Considering the high percentage of manganese in this sample C, the precipitation is interesting. In the case of D, much undissociated cementite and some peculiarly well-rounded nodules of annealing carbon appear in the matrix.

The following table gives the amount of free carbon found in these samples after quenching from 1050° C.:—

Sample.	After treatment.		
	Combined carbon.	Free carbon.	Carbon in austenite.
	per cent.	per cent.	per cent.
A	1·55	2·07	1·55
B	1·71	1·49	1·71
C	2·26	1·12	2·26
D	2·46	0·70	?

These experiments prove that the presence of the silicon in the carbide renders it less stable; that manganese and sulphur render the carbide more stable, but that at 1050° C. even 3·00 per cent. of manganese, or 0·45 per cent. of sulphur, fail to render the carbide stable.

The Precipitation of Annealing Carbon in Blister Steel.

The introduction of carbon into iron by cementation is of great interest. It will be found that Percy, in his book, discusses the subject to date, and the subsequent microscopical researches of Sorby and Arnold developed considerably our knowledge of the process.

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It is proposed, before discussing the precipitation of free carbon, first to consider the chemical physics of the process.

With regard to the percentage of carbon it is possible to introduce, Saniter introduced 2·9 per cent., whilst Charpy, confirming Marguerite's observations, introduced 6·72 per cent. by this process, Charpy using KCN and a temperature 650° C. In cementing bars of commercial sizes, it is impossible by means of charcoal to introduce more than an average percentage of 1·8 to 1·9 of carbon at the temperatures employed. It would seem from present experimental data to hand that iron carbide (Fe_3C) is synthetically produced at low temperatures when iron and carbon or some of its compounds are in contact, and it will be found, on examining the experimental data of the recorded instances of high percentages of carburizing, that they have all been performed on finely-divided iron, very fine wire, or drillings. If attempt is made to cement bar iron, say $3'' \times \frac{1}{2}''$, a very different set of conditions will be found; the iron and carbon in contact produce the carbide, but it is not until the temperatures at which diffusion* takes place are reached that the carburization can penetrate to the interior. Before the carbon can diffuse, the carbide must be in solution in the iron, and hence the degree to which the interior can be carburized is controlled by the solubility of the carbide. This solubility rises with the temperature, but at the temperatures normally employed, it seems, does not exceed 1·60 per cent. of carbon, even if Benedick's theory, elaborated by Howe,† is taken into consideration.

Such being the chemical physics involved in the cementation process, it is interesting to consider their bearing upon the precipitation of "annealing carbon" during such heat treatments.

Materials of the following composition were put through a somewhat drastic heat treatment. No. 1 is "washed iron," and contains 3·30 per cent. of carbon; the other four are high-class crucible steels of gradually increasing carbon content. The complete analyses were as follows:—

No.	Carbon.	Manganese.	Silicon.	Sulphur.	Phosphorus.
1	3·30	Trace	0·074	0·01	0·01
2	0·85	0·26	0·093	0·01	0·01
3	1·05	0·31	0·084	0·01	0·01
4	1·10	0·27	0·102	0·01	0·01
5	1·20	0·31	0·084	0·01	0·01

The bars were cemented with charcoal, seven days being required to attain the necessary heat of 950° to 1000° C.; they were then maintained between

* Arnold and McWilliam, 'J. Iron and Steel Institute,' 1899, vol. i.

† 'American Institution of Mining Engineers' Journal,' 1908.

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these temperatures for a period of five days, after which they slowly cooled during a further period of five days. Before the heat treatment, all the carbon in each of the bars was in the combined state; the analyses after the treatment are of considerable interest, and are given in the next table:—

No.	Total carbon.	Annealing carbon.	Combined carbon.	Gain in carbon.
1	3·30	3·15	0·15	Nil
2	1·54	0·10	1·44	0·69
3	1·46	0·26	1·20	0·41
4	1·50	0·88	0·62	0·40
5	1·60	1·00	0·60	0·40

It will thus be seen that in this instance a precipitation of free carbon was obtained, and it will be observed that the higher the initial carbon percentage the higher the free carbon.

Before discussing further this set of results, the author considers it better to present another set of experiments which were made in collaboration with Mr. Albert Senior. Bars of pure Swedish wrought iron were normally cemented five times at a temperature of 1050° to 1100° C., at which maximum temperature they were maintained in each case for about 12 days.

The carbon percentages thus introduced are recorded in the following table:—

	Total carbon.	Combined carbon.	Annealing carbon.
After first cementation.....	1·28	1·28	Nil
„ second „	1·43	1·43	„
„ third „	1·50	1·16	0·34
„ fourth „	1·49	0·53	0·96
„ fifth „	1·68	0·71	0·95

It will be seen that it was not until the third drastic heating that any free carbon in this instance appeared, but that the fourth heat treatment precipitated 0·96 per cent. of it. In the earlier experiment, however, a precipitation was obtained in a single cementation at 950° to 1000° C. in bars having after exposure to the temperature 1·50 to 1·60 per cent. carbon.

In Plate 4, fig. 28, will be seen the microstructure of No. 1 of the first series; it will be seen to consist of a matrix of laminated pearlite in which are embedded the annealing carbon nodules in ferrite envelopes. In figs. 29 to 32, Plate 4, will be seen the structures of the other four bars. Bar 2 showed a typical cemented bar structure of cementite and pearlite, in Bar 3 here and there the cementite had decomposed with resulting

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annealing carbon as seen in the micrograph, whilst in Bars 4 and 5 all the carbon of supersaturation, *i.e.* all the free massive carbide, has been dissociated into free carbon and iron.

Turning now to the second series of experiments, on Plate 5, fig. 33, will be found an illustration of their microstructure after the first cementation; in this instance the cementite of the pearlite has been balled up; after the second cementation the structure was much the same. On examination of the bars after the third heat treatment the massive cementite had broken down apparently *in situ*, see fig. 34. After the fifth cementation, it was found that all the carbon of supersaturation had been precipitated and that the structure, as shown in fig. 35, Plate 5, merely presented a pearlite matrix in which the annealing carbon appeared in the usual manner enveloped in ferrite.

In the first set of experiments free carbon was precipitated, and roughly in proportion to the carbon of supersaturation present in the original bar. It would therefore appear that the original cementite was in some manner the cause of the action; as to what this action was is not clear, as, each bar having absorbed more carbon, it would appear that this free cementite must for the most part have been redissolved in the "austenite." Owing to the comparatively low temperature, however, it is most likely that some outstanding islands of carbide would be subjected to the temperature of the treatment. As shown earlier, the carbide of iron is very unstable when temperatures approximating to 1000° C. are reached, and hence it is likely would thus dissociate. The second series support this theory, because, on heating up to 1050° to 1100° C., a further 100° C., no precipitation was obtained until the third heating, and then it would only appear to consist of a local breaking down of the massive cementite, as shown in fig. 34, Plate 5. The increase in temperature would tend to prevent the cementite remaining undissolved in the "austenite," owing to the increased solubility of the carbide with this rising temperature.

The Precipitation of Annealing Carbon in Ordinary Steels.

It is now proposed to discuss the problem of the black steels of commerce in the light of experiments previously recorded. Dr. Arnold and Prof. McWilliam, in their paper on the "Thermal Transformations of Carbon Steel," record some interesting data and also an equally interesting explanation. They point out that it is only in steels which are supersaturated that the precipitation is likely to be observed. This the author confirms, as he has never met the phenomenon except in steels which normally present a microstructure in which free cementite occurs.

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The author found that when the annealing carbon was produced by simple heat treatment a formation of microstructure similar to fig. 35, Plate 5, was obtained, and such is the general appearance of annealing carbon when produced in this manner.

If free carbon be produced by working and rolling at low temperatures the author finds that a very different microstructure is presented. In figs. 9 and 10, Plate 2, will be seen the microstructures of such a bar; fig. 9 represents the structure of the normal portion of the bar; fig. 10 illustrates the form which the free carbon takes. The author's theory is, that in such an instance the cementite membranes as such have decomposed and then drawn in and decomposed the cementite produced by resolution of the pearlite. Intense pressure and friction reasonably might be expected to commence such an action, which, once commenced, might run some distance through the material, thus accounting for this dissociation of the carbide.

With regard to the hypothesis put forth by Arnold and McWilliam* as to the chemical physics involved in the precipitation during the annealing process, the author with deference to those workers would presume to take some exception. They state that "during the slow cooling from 1000° C. the dissolved cementite completely fell out at about 900° C., and from this temperature downwards gradually segregated into nodular masses. Afte the A.R. 1 2 3 change point, the pearlite gradually became laminated. Then, acting over a certain radius of molecular attraction, the A or cementite carbide drew in about half the B or pearlite carbide, thus augmenting its own mass, and leaving round it a large mass of crystalline ferrite, the outer boundaries of which mark the radius of action through which the nodules of cementite asserted their attraction on the striæ of B carbide in the laminated pearlite. Then, for some reasons which the authors cannot specify, the whole of the segregated masses of Fe_3C decomposed into amorphous carbon and iron, the latter augmenting the crystalline ferrite surrounding the free carbon masses."

In the light of the author's work already recorded, he would suggest that, in the instance to which reference has just been made, the whole of the cementite would possibly not be in solution at the high temperatures. As previously suggested, any structurally free carbide, on exposure to the temperature of 1000° C. for such a period, would tend to dissociate, and, as during the slow cooling the cementite gradually precipitated, it would by nucleus action be drawn into the regions of chemical activity, and be progressively decomposed. The fact that the size, shape and position of the subsequent "annealing" carbon bear no relation to the similar features of

* 'Journal Iron and Steel Institute,' 1905.

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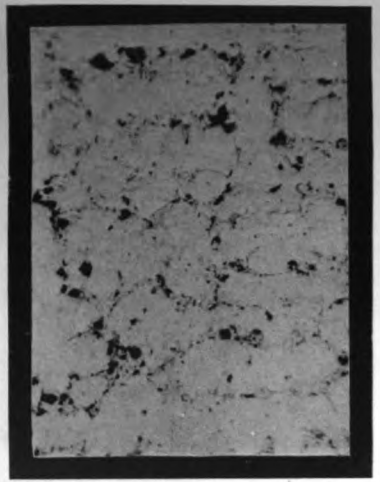

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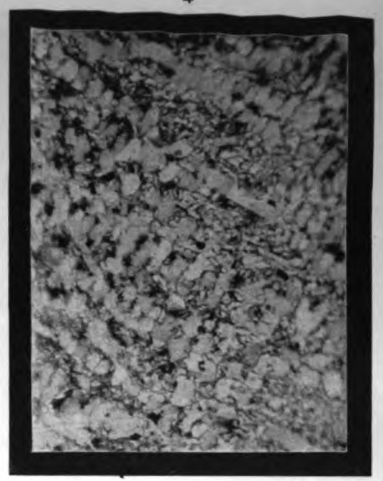

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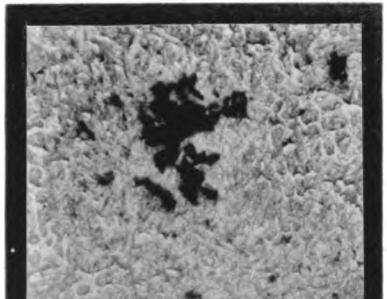

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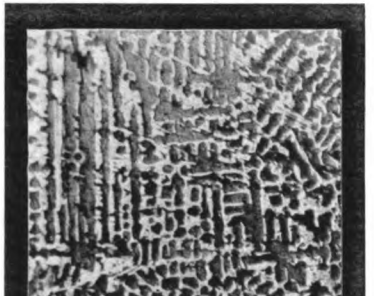

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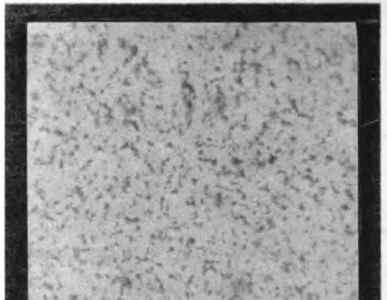

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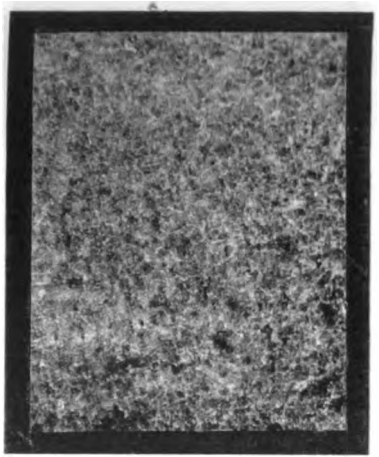

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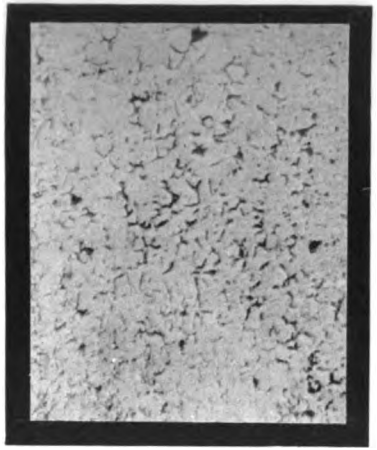

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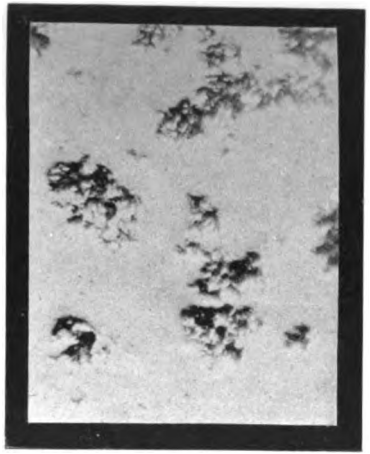

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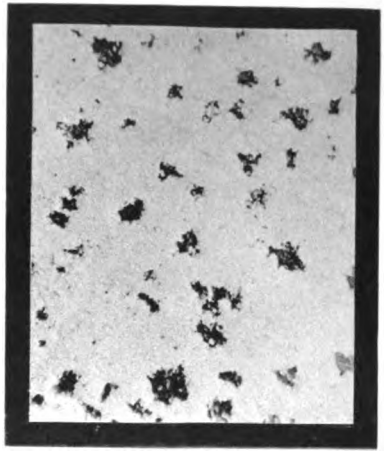

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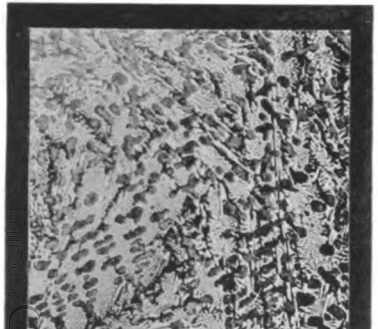

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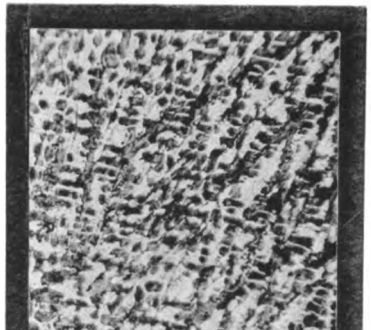

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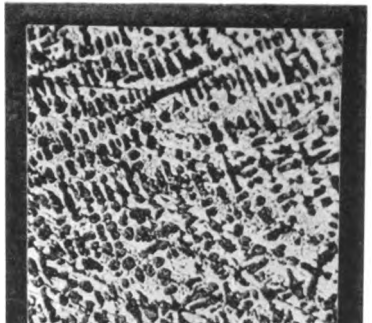

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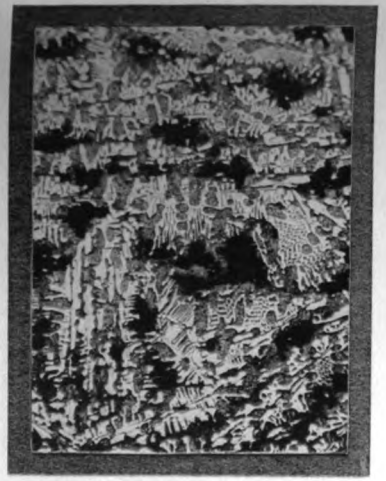

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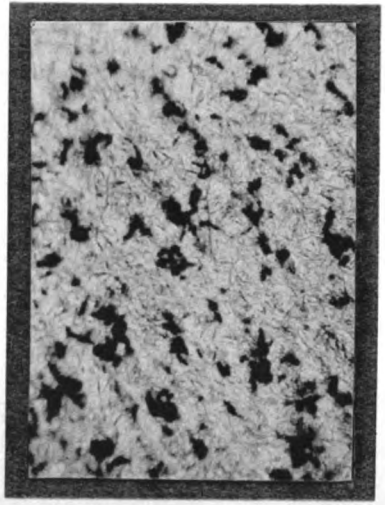

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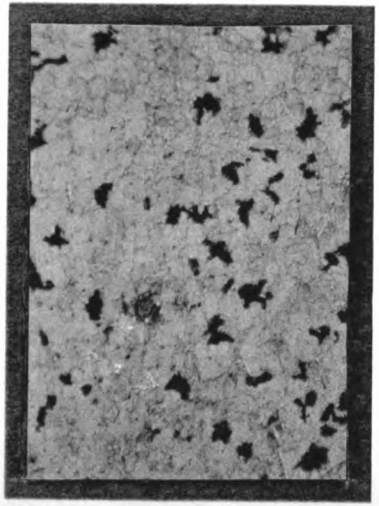

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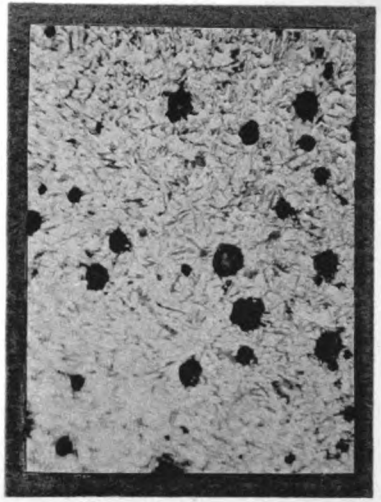

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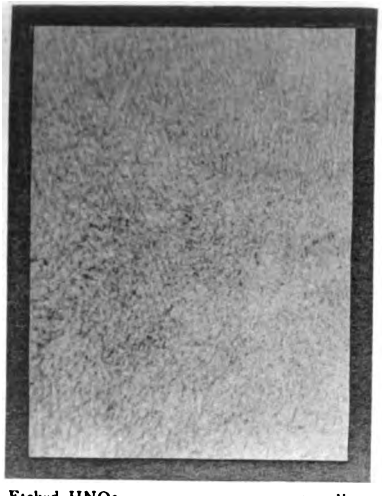

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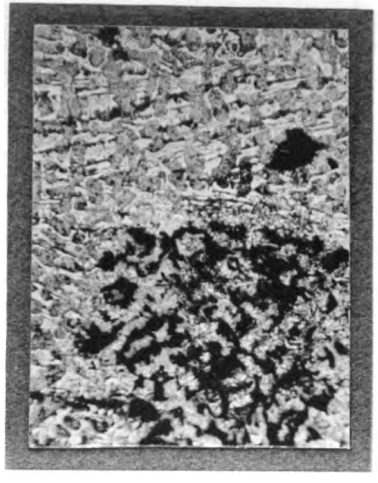

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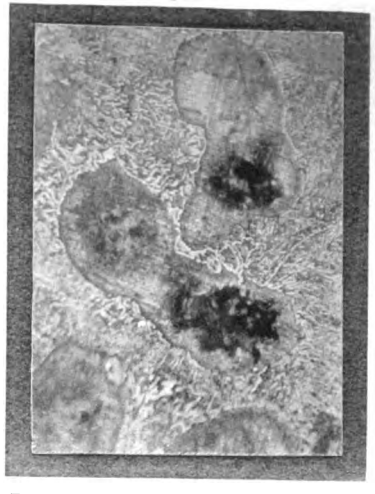

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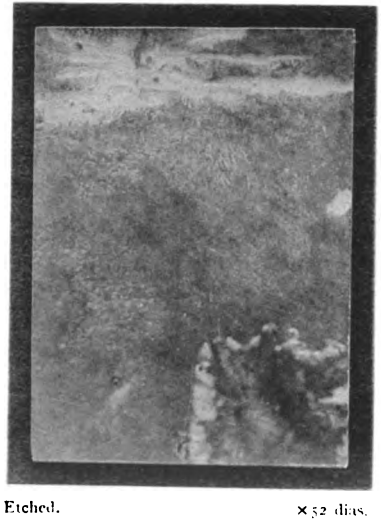

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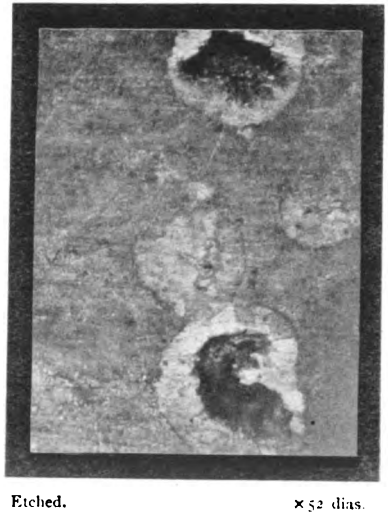

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the cementite in such a steel in the normal cementite-pearlite condition supports this view.

That the whole of the carbide decomposes in the region of A.R. 1 2 3, as suggested by Arnold and McWilliam, the author considers to be unlikely, since, unless the action has begun at high temperatures, his experiments prove the stability of iron carbide (Fe_3C) at such a low temperature under a simple heat treatment.

It would thus seem that there is always a possibility of the production of black steel when free cementite is present, and that only by the addition to the steels of elements which will produce a stable carbide can the difficulty be overcome. In the normal iron-carbon steels of commerce if the annealing or working is not conducted at a temperature at which the cementite is dissolved in the austenite there is always a danger of this phenomenon.

The author would like before closing to thank Dr. W. M. Hicks for the very kind interest he has taken in the research, and also to associate with it the names of Mr. J. F. Crowley and Prof. A. McWilliam, who have also wherever possible rendered valuable assistance to him in the prosecution of his research.

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On the Fourier Constants of a Function.

By W. H. Young, Sc.D., F.R.S.

(Received December 10, 1910,—Read January 26, 1911.)

§ 1. Considerable progress has been made lately in the study of the properties of the constants in a Fourier series, using this term in the most general sense possible consistent with the extended definition of integration due to Lebesgue. Thus we now know that these coefficients necessarily under all circumstances have the unique limit zero,* as the integer denoting their place in the series increases indefinitely, and that the same is true if we substitute for that integer any other quantity which increases without limit. Further, we know that the series whose general term is b_n/n, where b_n is the typical coefficient of the sine terms, always converges, and we are able to write down its sum.† That the series whose general term is a_n, where a_n is the typical coefficient of the cosine terms, converges when the origin is an internal point of an interval throughout which the function has bounded variation, and that accordingly the series whose general term is a_n/n^q, $(0<q)$, converges, is an immediate consequence of known results. Should the function have its square summable,‡ we know§ that the series whose general term is $(a_n^2+b_n^2)$ converges, and we can write down its sum. We can also sum the series of the products of the Fourier coefficients of two such functions. From the property that $\Sigma(a_n^2+b_n^2)$ converges, we can deduce that the series $\Sigma a_n/n^q$ and $\Sigma b_n/n^q$, $(\frac{1}{2}<q)$, necessarily converge absolutely.

Again, making use of a theorem recently proved,‖ we may integrate the Fourier series of any summable function, after multiplying it term by term by any function of bounded variation, with a certainty that we shall obtain the same result as if the Fourier series converged to the function to which it corresponds, and such term-by-term integration were allowable.

Choosing for the function of bounded variation in question various simple

* B. Riemann, "Ueber die Darstellbarkeit einer Function durch eine trigonometrische Reihe," § 10, 'Ges. Werke,' 2nd edition, 1854, p. 254; H. Lebesgue, 'Leçons sur les séries trigonométriques," 1906, p. 61.

† H. Lebesgue, *loc. cit.*, § 53, p. 102.

‡ A function is, in accordance with the usage now accepted, said to be summable when it possesses a Lebesgue integral proper or improper. This has superseded the nomenclature in Hobson's 'Treatise on the Theory of Functions of a Real Variable.'

§ P. Faton, 'Séries trigonométriques et séries de Taylor," 'Acta. Math.,' 1905, vol. 30, pp. 335—400.

‖ W. H. Young, "On the Integration of Fourier Series," 1910, presented to the L.M.S.

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functions we shall obtain the sums of a number of series involving the Fourier coefficients of any summable function.

By using the other theorems in the paper last cited we obtain other results of a less general character.

In the present note I propose to employ the theorems of that paper to prove the following properties of the coefficients:—

(1) Whatever be the nature of the summable function $f(x)$, provided only that in the neighbourhood of the origin it is of bounded variation, then not only as is obvious the series of the a_n's, but also the series of the b_n's, is convergent when the individual terms of the series are divided by any the same positive power, however small, of the integer denoting the place of the coefficient in the Fourier series; further, the sums of the series are expressible as simple integrals.*

(2) Whatever be the nature of the summable function $f(x)$, provided only that in the neighbourhood of the origin its square is summable, the same property holds good, so long as the index of the power of the dividing integer is greater than $\frac{1}{2}$; the sums of the series are of the same form as in (1).

(3) If in the neighbourhood of the origin we can only assert that the function is bounded, the statement remains true if we interpret the terms "convergence" and "sum" both in the Cesaro sense.

(4) If in the neighbourhood of the origin one of the three preceding conditions holds, while in the rest of the interval $(-\pi, \pi)$ $f(x)$ possesses a Harnack-Lebesgue integral, the corresponding statement is true, if we interpret the terms "convergence" and "sum" in the Cesaro sense. The Fourier series is then a generalised one.

Closely associated with the first of these four statements is the following which is also proved below:—

(1 *bis*) Whatever be the nature of the summable function $f(x)$, provided that in some interval containing the origin the function $[f(x)-f(-x)]/x$ is summable, the series whose general term is $n^{-q}b_n$, $(0 \leq q < 1)$, is convergent; if, on the other hand, for some value of the constant C, the function $[f(x)+f(-x)-C]/x$ is summable in some interval containing the origin, the series whose general term is $n^{-q}a_n$, $(0 < q < 1)$, is convergent; in both cases it is to be supposed that in the rest of the interval $(-\pi, \pi)$ the function $f(x)$ is summable. Moreover, the formulæ for the sums have the same form as in (1).

The first part of the statement (1 *bis*) just made contains a result which seems to have a special interest of its own. As is well known, the series

* See below § 3, formulæ I and II; § 5, formula III; § 6, formula IV; §§ 7 and 8.

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whose general term is a_n converges, and has $\frac{1}{2}[f(+0)-f(-0)]$ for its sum when $f(x)$ is a function of bounded variation. The result in question is what may accordingly be called the companion result, namely,* that the series whose general term is b_n converges, and has $\frac{1}{\pi}\int_0^\infty \frac{f(x)-f(-x)}{x}\,dx$ for its sum, provided only that this integral exists. Here it must be recollected that $f(x)$ has been made periodic in the usual way, so that the integral in question certainly exists between any limits of integration which do not contain the origin between them; thus the only limitation of the nature of the function $f(x)$ relates to the neighbourhood of the origin.

The results have all been stated with reference to the coefficients and not to the Fourier series itself. It should, however, be hardly necessary to remark that, by transforming the origin, we obtain corresponding results relating to the Fourier series itself, and to its very important, up to the present almost entirely neglected, companion series, got from it by interchanging the coefficients of the sine and cosine terms, and changing the sign of the latter. In particular we have in this way the sum of the companion series, when a certain function is summable; we can also find the function of which this series is the Fourier series in an important class of cases, in which we know it to be a Fourier series. I reserve for subsequent publication the further development of this remark.

In conclusion I would add that the formulæ obtained may be generalised in a variety of ways by means of the theorems here utilised. The present paper, however, contains the complete solution, within the limits proposed, of the problem with which we started, thus illustrating the usefulness of the theorems in the paper so frequently quoted.

§ 2. Denote by $f_1(x)$ the function which is zero at the extremities of the interval $(-\pi, \pi)$, and which, inside this interval, is equal to the expression

$$\tfrac{1}{2}[f(x)+f(-x)]-\frac{1}{4\pi}\int_{-\pi}^{\pi}[f(x)+f(-x)]\,dx,$$

while, outside this interval, such values are to be assigned to $f_1(x)$ as to make it periodic, with period 2π.

Denote by $f_2(x)$ the function got from $f_1(x)$ by changing $f(-x)$ into $-f(-x)$. Then evidently $f_1(x)$ and $f_2(x)$ are summable, have their squares summable, are bounded, or of bounded variation, in a neighbourhood containing the origin, if $f(x)$ possesses these respective properties.

Further, since $\int_{-\pi}^{\pi} f_1(x)\,dx$ and $\int_{-\pi}^{\pi} f_2(x)\,dx$ are both zero, it is clear that the

* § 9, formula V.

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indefinite integrals of $f_1(x)$ and $f_2(x)$ will all be periodic, and accordingly oscillate finitely as the upper limit of integration approaches infinity.

Again, as we have just seen, the Fourier series corresponding to $f_1(x)$ and $f_2(x)$ will be deficient of constant term. Moreover,

$$\int_{-\pi}^{\pi} f_1(x) \cos nx\, dx = \tfrac{1}{2}\int_{-\pi}^{\pi} [f(x)+f(-x)-c_1] \cos nx\, dx = \int_{-\pi}^{\pi} f(x) \cos nx\, dx = a_n,$$

where c_1 is a constant.

Also $$\int_{-\pi}^{\pi} f_1(x) \sin nx\, dx = \tfrac{1}{2}\int_{-\pi}^{\pi} [f(x)+f(-x)-c_1] \sin nx\, dx = 0.$$

Similarly, $$\int_{-\pi}^{\pi} f_2(x) \cos nx\, dx = 0, \qquad \int_{-\pi}^{\pi} f_2(x) \sin nx\, dx = b_n.$$

§ 3. We first consider the case where $f(x)$ has bounded variation in the neighbourhood of the origin, and the index q of the power to which the integer n is raised lies between zero and unity, the extreme values not included.

Put $g(x) = x^{q-1}$, where $0<q<1$, and consider the integral $\int_0^{\infty} g(x) f_1(x)\, dx$. Except in the neighbourhood of the origin, $g(x)$ is a function of bounded variation in the whole infinite interval, and has, as x increases indefinitely, the unique limit zero. Moreover, $f_1(x)$ is such that $\int_k^x f_1(x)\, dx$ is a periodic function of x which oscillates finitely in the whole infinite interval (k, ∞). Hence, by the extension to infinity of the theorem cited in § 1, $\int_k^{\infty} g(x) f_1(x)\, dx$ is the sum of the series of integrals got by integrating, between the limits k and infinity, the successive terms of the Fourier series of $f_1(x)$, after having previously multiplied them by $g(x)$.

Next consider $\int_0^k g(x) f_1(x)\, dx$. In the interval of integration $g(x)$ is summable, while $f_1(x)$ has bounded variation, provided our choice of k has been a suitable one, which we may suppose to be the case. To this integral we may apply the theorem already cited in its simple form, so that we see that it is equal to the sum of the series of integrals got by integrating between the limits 0 and k the successive terms of the Fourier series of $f_1(x)$, after having previously multiplied them by $g(x)$.

Adding the two results so obtained, and bearing in mind that the Fourier series of $f_1(x)$ has no sine terms, we have

$$\int_0^{\infty} x^{q-1} f_1(x)\, dx = \sum_{n=1}^{\infty} a_n \int_0^{\infty} x^{q-1} \cos nx\, dx.$$

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Similarly $$\int_0^\infty x^{q-1} f_2(x)\,dx = \sum_{n=1}^{\infty} b_n \int_0^\infty x^{q-1} \sin nx\,dx.$$

Hence, since we know that, when $0 < q < 1$,

$$\int_0^\infty x^{q-1} \cos x\,dx = \Gamma(q) \cos \tfrac{1}{2} q\pi \quad \text{and} \quad \int_0^\infty x^{q-1} \sin x\,dx = \Gamma(q) \sin \tfrac{1}{2} q\pi,$$

we get

$$\int_0^\infty x^{q-1} f_1(x)\,dx = \sum_{n=1}^{\infty} a_n \int_0^\infty \left(\frac{x}{n}\right)^{q-1} \cos x\, d\left(\frac{x}{n}\right) = \sum_{n=1}^{\infty} \frac{a_n}{n^q} \int_0^\infty x^{q-1} \cos x\,dx$$

$$= \cos \tfrac{1}{2} q\pi \Gamma(q) \sum_{n=1}^{\infty} n^{-q} a_n. \qquad \text{(I)}$$

Similarly $$\int_0^\infty x^{q-1} f_2(x)\,dx = \sin \tfrac{1}{2} q\pi\, \Gamma(q) \sum_{n=1}^{\infty} n^{-q} b_n. \qquad \text{(II)}$$

§ 4. Before going on to obtain the corresponding formulæ when q is not internal to the interval (0, 1), we remark that the results above obtained are obviously true, *mutatis mutandis*, when near the origin $f(x)$ is respectively bounded, or has its square summable. In the former case the above argument is unaffected, provided only we interpret the words "sum" and "convergence" of a series in the Cesaro manner. In fact, the reasoning for the interval (k, ∞) applies, as before, as all that was required of $f(x)$ in that interval was that it should be summable in every finite portion of it. As regards the interval $(0, k)$, the theorem used is still applicable, as is shown in the paper quoted, with the proviso in question.

If, on the other hand, all we know of $f(x)$, and therefore of $f_1(x)$ and $f_2(x)$, in the neighbourhood of the origin, is that its square is summable, we need the summability of the square of $g(x)$ in the interval $(0, k)$. This requires q to be greater than $\frac{1}{2}$. With this understanding, therefore, our results are still true.

If, finally, we only know of $f(x)$ near $x = \pi$ or $-\pi$ that it possesses a Harnack-Lebesgue integral, the corresponding portion of the integrals will in general only converge in the Cesaro way.* Hence in this case, even if $f(x)$ is of bounded variation near the origin, the final series can only be summed in general in the Cesaro way.

§ 5. Let us now make the hypothesis that q is unity. By the theory of the integration of Fourier series, we have, if $F_1(x)$, $F_2(x)$, denote any definite integrals of $f_1(x), f_2(x)$,

$$F_1(x) = \text{const.} + \sum_{n=1}^{\infty} n^{-1} a_n \sin nx,$$

$$F_2(x) = \text{const.} - \sum_{n=1}^{\infty} n^{-1} b_n \cos nx.$$

* "On the Integration of Fourier Series," § 7.

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The first equation gives us no information, the second equation tells us that

$$\sum_{n=1}^{\infty} n^{-1} b_n = \text{const.} - F_2(0) = \frac{1}{2\pi}\int_{-\pi}^{\pi} F_2(x)\,dx - F_2(0). \qquad \text{(III)}$$

Here the summation must be supposed performed in the Cesaro manner, when the Fourier series is a generalised one.*

This result is due to Lebesgue,† in the case when the Fourier series is an ordinary one.

§ 6. To obtain the sum of the series whose general term is $n^{-1}a_n$, we must adopt a different method. We require to use the fact that, in the neighbourhood of the origin, $f(x)$ has, under all the circumstances supposed, its square summable. On the other hand the function

$$\tfrac{1}{2}\log\tfrac{1}{4}\operatorname{cosec}^2\tfrac{1}{2}x$$

has, except in the neighbourhood of the origin, bounded variation throughout the interval $(-\pi, \pi)$. In the neighbourhood of the origin it has its square summable—in fact, $\log x - \log\sin x < \log(1+\frac{1}{6}x)^2 < x^2/6 < x^2$.

Therefore, $\qquad (\log\operatorname{cosec} x)^2 < x^4 - 2x^2\log x + (\log x)^2.$

Hence, also, the square of the function in question, $\frac{1}{2}\log\frac{1}{4}\operatorname{cosec}^2\frac{1}{2}x$, is less than a summable function.

Thus the interval $(-\pi, \pi)$ can be broken up into two parts, in one of which one of the two functions $f_1(x)$ and $\frac{1}{2}\log\frac{1}{4}\operatorname{cosec}^2\frac{1}{2}x$ is of bounded variation and the other is summable, while in the remaining part both the functions have their squares summable. Applying, therefore, the theorems already referred to, to these separate portions, and adding the results, we get

$$\int_{-\pi}^{\pi} f_1(x)\,\tfrac{1}{2}\log\tfrac{1}{4}\operatorname{cosec}^2\tfrac{1}{2}x\,dx = \sum_{n=1}^{\infty} n^{-1}a_n, \qquad \text{(IV)}$$

since the generic Fourier constant of the function $\frac{1}{2}\log\frac{1}{4}\operatorname{cosec}^2\frac{1}{2}x$ is n^{-1}.‡

Here we have assumed $f(x)$ to be summable. If, in any portion of the interval $(-\pi, \pi)$, it have only a Harnack-Lebesgue integral, the argument still applies, provided we sum the series in the Cesaro way.

§ 7. Since the function corresponding to an integrated Fourier series is an integral, it is, of course, a continuous function, and belongs also, *a fortiori*, to the class of functions whose square is summable. Accordingly,

* W. H. Young, "On the Conditions that a Trigonometrical Series should have the Fourier Form," 1910. Supplementary Note. Presented to the London Mathematical Society.

† *Loc. cit.*

‡ D. Bernoulli, 'Petrop. N. Comm.,' 1772. See Hobson's 'Theory of Functions of a Real Variable,' p. 639.

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the method of § 6 enables us to sum the series, whose general terms are respectively

$$n^{-2}b_n,\ n^{-3}a_n\ldots,$$

where a_n and b_n are the Fourier constants of any summable function whatever. The formulæ, of course, closely resemble that obtained at the conclusion of that article.

On the other hand, the series whose general terms are

$$n^{-2}a_n,\ n^{-3}b_n\ldots,$$

where, again, a_n and b_n are the Fourier constants of any summable function whatever, are obtained by mere repetition of the process employed in §5, their sums having a form which closely resembles that of the series summed in that article.

§ 8. The case in which q is greater than unity, and not an integer, alone remains to be considered. The method to be adopted is obvious. We have only to apply to the integrated series the reasoning of § 3, with this simplification, that the function to which the Fourier series corresponds, being now an integral of $f_1(x)$, or of $f_2(x)$, as the case may be, is certainly of bounded variation in the case of an ordinary Fourier series, and at least continuous in the case of a generalised Fourier series in every finite interval, so that no special hypothesis is needed. The formulæ are easily obtained.

§ 9. To write down (by request) the formulæ referred to in §§ 7 and 8, it is convenient to use the following notation :—

$$f_1(x) = \tfrac{1}{2}\{f(x)+f(-x)\} - \frac{1}{2\pi}\int_0^\pi \{f(x)+f(-x)\}\,dx,$$

$$f_2(x) = \tfrac{1}{2}\{f(x)-f(-x)\},$$

$$\mathrm{F}_1(x) = \int_0^x f_1(x)\,dx, \qquad \mathrm{F}_2(x) = \int_0^x f_2(x)\,dx,$$

$$\mathrm{G}_1(x) = \int_0^x \mathrm{F}_1(x)\,dx, \qquad \mathrm{G}_2(x) = \int_0^x \left\{\mathrm{F}_2(x) - \frac{1}{\pi}\int_0^\pi \mathrm{F}_2(x)\,dx\right\}dx,$$

$$\mathrm{H}_1(x) = \int_0^x \left\{\mathrm{G}_1(x) - \frac{1}{\pi}\int_0^\pi \mathrm{G}_1(x)\,dx\right\}dx, \qquad \mathrm{H}_2(x) = \int_0^x \mathrm{G}_2(x)\,dx,$$

$$\mathrm{K}_1(x) = \int_0^x \mathrm{H}_1(x)\,dx, \qquad \mathrm{K}_2(x) = \int_0^x \mathrm{H}_2(x)\,dx,$$

and so on.

We then have the following formulæ, which are those given in § 5 and the analogous formulæ referred to at the end of §7 :—

$$f_1(x) \sim \sum_{n=1}^{\infty} a_n \cos nx, \qquad f_2(x) \sim \sum_{n=1}^{\infty} b_n \sin nx, \qquad \mathrm{F}_1(x) = \sum_{n=1}^{\infty} n^{-1}a_n \sin nx,$$

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$$F_2(x) - \frac{1}{\pi}\int_0^\pi F_2(x)\,dx = -\sum_{n=1}^{\infty} n^{-1}b_n \cos nx, \quad \text{thus} \quad \sum_{n=1}^{\infty} n^{-1}b_n = \frac{1}{\pi}\int_0^\pi F_2(x)\,dx,$$

$$G_1(x) - \frac{1}{\pi}\int_0^\pi G_1(x)\,dx = -\sum_{n=1}^{\infty} n^{-2}a_n \cos nx, \quad \text{thus} \quad \sum_{n=1}^{\infty} n^{-2}a_n = \frac{1}{\pi}\int_0^\pi G_1(x)\,dx,$$

$$G_2(x) = -\sum_{n=1}^{\infty} n^{-2}b_n \sin nx, \qquad H_1(x) = -\sum_{n=1}^{\infty} n^{-3}a_n \sin nx,$$

$$H_2(x) - \frac{1}{\pi}\int_0^\pi H_2(x)\,dx = \sum_{n=1}^{\infty} n^{-3}b_n \cos nx, \quad \text{thus} \quad \sum_{n=1}^{\infty} n^{-3}b_n = -\frac{1}{\pi}\int_0^\pi H_2(x)\,dx,$$

$$K_1(x) - \frac{1}{\pi}\int_0^\pi K_1(x)\,dx = \sum_{n=1}^{\infty} n^{-4}a_n \cos nx, \quad \text{thus} \quad \sum_{n=1}^{\infty} n^{-4}a_n = -\frac{1}{\pi}\int_0^\pi K_1(x)\,dx,$$

$$K_2(x) = \sum_{n=1}^{\infty} n^{-4}b_n \sin nx,$$

and so on.

The formula obtained in § 6,

$$\int_{-\pi}^{\pi} f_1(x)\,\tfrac{1}{2}\log\tfrac{1}{4}\operatorname{cosec}^2\tfrac{1}{2}x\,dx = \sum_{n=1}^{\infty} n^{-1}a_n,$$

may evidently be written

$$2\int_0^\pi f_1(x)\log\tfrac{1}{2}\operatorname{cosec}\tfrac{1}{2}x\,dx = \sum_{n=1}^{\infty} n^{-1}a_n.$$

Similarly, without any restriction on $f(x)$, with the notation just explained, bearing in mind that $\int_0^\pi \log\tfrac{1}{2}\operatorname{cosec}\tfrac{1}{2}x\,dx = 0$, we have the analogous formulæ referred to at the beginning of § 7 :—

$$2\int_0^\pi F_2(x)\log\tfrac{1}{2}\operatorname{cosec}\tfrac{1}{2}x\,dx = -\sum_{n=1}^{\infty} n^{-2}b_n,$$

$$2\int_0^\pi G_1(x)\log\tfrac{1}{2}\operatorname{cosec}\tfrac{1}{2}x\,dx = -\sum_{n=1}^{\infty} n^{-3}a_n,$$

$$2\int_0^\pi H_2(x)\log\tfrac{1}{2}\operatorname{cosec}\tfrac{1}{2}x\,dx = \sum_{n=1}^{\infty} n^{-4}b_n,$$

$$2\int_0^\pi K_1(x)\log\tfrac{1}{2}\operatorname{cosec}\tfrac{1}{2}x\,dx = \sum_{n=1}^{\infty} n^{-5}a_n,$$

and so on.

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The formulæ referred to in § 8, in which $0 < q < 1$, are then as follows:—

$$\int_0^\infty x^{q-1} F_1(x)\,dx = \sin \tfrac{1}{2} q\pi\, \Gamma(q) \sum_{n=1}^{\infty} n^{-q-1} a_n,$$

$$\int_0^\infty x^{q-1}\left[F_2(x) - \frac{1}{\pi}\int_0^\pi F_2(x)\,dx\right]dx = -\cos \tfrac{1}{2} q\pi\, \Gamma(q) \sum_{n=1}^{\infty} n^{-q-1} b_n,$$

$$\int_0^\infty x^{q-1}\left[G_1(x) - \frac{1}{\pi}\int_0^\pi G_1(x)\,dx\right]dx = -\cos \tfrac{1}{2} q\pi\, \Gamma(q) \sum_{n=1}^{\infty} n^{-q-2} a_n,$$

$$\int_0^\infty x^{q-1} G_2(x)\,dx = -\sin \tfrac{1}{2} q\pi\, \Gamma(q) \sum_{n=1}^{\infty} n^{-q-2} b_n,$$

$$\int_0^\infty x^{q-1} H_1(x)\,dx = -\sin \tfrac{1}{2} q\pi\, \Gamma(q) \sum_{n=1}^{\infty} n^{-q-3} a_n,$$

$$\int_0^\infty x^{q-1}\left[H_2(x) - \frac{1}{\pi}\int_0^\pi H_2(x)\,dx\right]dx = \cos \tfrac{1}{2} q\pi\, \Gamma(q) \sum_{n=1}^{\infty} n^{-q-3} b_n,$$

$$\int_0^\infty x^{q-1}\left[K_1(x) - \frac{1}{\pi}\int_0^\pi K_1(x)\,dx\right]dx = \cos \tfrac{1}{2} q\pi\, \Gamma(q) \sum_{n=1}^{\infty} n^{-q-4} a_n,$$

$$\int_0^\infty x^{q-1} K_2(x)\,dx = \sin \tfrac{1}{2} q\pi\, \Gamma(q) \sum_{n=1}^{\infty} n^{-q-4} b_n,$$

and so on.

§ 10. We now assume that $\{f(x)-f(-x)\}/x$ is summable in an interval containing the origin, and proceed to prove the results (1 *bis*) of the introduction.

Since $[f(x)-f(-x)]/x$ is, by hypothesis, a summable function, so is $[f(x)-f(-x)]/\sin x$. Also $\sin x/x$ is a function of bounded variation in any finite interval $(0, k)$. Hence, using the theorem so often quoted, and denoting by πA_n the integral $\int_{-\pi}^{\pi} [f(x)-f(-x)] \operatorname{cosec} x \cos nx\,dx$, we have

$$\int_0^k \frac{f(x)-f(-x)}{\sin x} \cdot \frac{\sin x}{x}\,dx = \tfrac{1}{2}\int_0^k A_0 \frac{\sin x}{x}\,dx + \sum_{n=1}^{\infty} \int_0^k A_n \frac{\cos nx \sin x}{x}\,dx; \quad (1)$$

so that, in particular, the series on the right-hand side converges.

Now the summation on the right-hand side of the preceding equation is the unique limit when m increases indefinitely of the following:—

$$\tfrac{1}{2}\sum_{n=1}^{m} \int_0^k A_n \frac{\sin(n+1)x - \sin(n-1)x}{x}\,dx = -\tfrac{1}{2} A_2 \int_0^k \frac{\sin x}{x}\,dx$$

$$+ \tfrac{1}{2} A_{m-1} \int_0^k \frac{\sin mx}{x}\,dx + \tfrac{1}{2} A_m \int_0^k \frac{\sin(m+1)x}{x}\,dx$$

$$+ \tfrac{1}{2}\sum_{n=1}^{m-2} (A_n - A_{n+2}) \int_0^k \frac{\sin(n+1)x}{x}\,dx. \quad (2)$$

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But $$A_n - A_{n+2} = \frac{1}{\pi}\int_{-\pi}^{\pi} 2[f(x)-f(-x)]\sin(n+1)x\,dx = 4b_{n+1}.$$

Hence (1) becomes

$$\tfrac{1}{2}\int_0^k \frac{f(x)-f(-x)}{x}dx = \sum_{n=1}^{\infty}\int_0^k b_n \frac{\sin nx}{x}dx, \tag{3}$$

for in (2) the second and third terms on the right vanish when we proceed to the limit, since A_{m-1} and A_m, being the Fourier coefficients of a summable function, have zero as unique limit when m increases indefinitely, while the integrals by which they are multiplied are always numerically less than π. But, by the usual argument,

$$\tfrac{1}{2}\int_k^{\infty} \frac{f(x)-f(-x)}{x}dx = \sum_{n=1}^{\infty}\int_k^{\infty} b_n \frac{\sin nx}{x}dx. \tag{4}$$

Hence, adding (3) and (4), and using the fact that $\int_0^{\infty}\frac{\sin nx}{x}dx = \frac{\pi}{2}$, we have

$$\tfrac{1}{2}\int_0^{\infty} \frac{f(x)-f(-x)}{x}dx = \frac{\pi}{2}\sum_{n=1}^{\infty} b_n,$$

which may, if $f(x)/x$ is summable, be written in the form

$$\frac{1}{\pi}\int_{-\infty}^{\infty} \frac{f(x)}{x}dx = \sum_{n=1}^{\infty} b_n. \tag{V}$$

§ 11. A slight modification of the argument used in the preceding article enables us to show that our formulæ (1) and (2) hold on the new hypothesis of the introduction, q lying, as before, in the open interval (0, 1). In formula (2) we require $f_2(x)/x$ to be summable in the neighbourhood of the origin, while in formula (I) the condition is that $(f_1(x)-C)/x$ should for some value of the constant C be summable in the neighbourhood of the origin.

To prove this we work with the factor $x^{q-1}\sin x$, instead of $x^{-1}\sin x$, and arrive, by the same reasoning as in § 10, at the equation corresponding to (3), viz.:—

$$\tfrac{1}{2}\int_0^k x^{q-1}[f(x)-f(-x)]\,dx = \sum_{n=1}^{\infty}\int_0^k b_n x^{q-1}\sin nx\,dx.$$

Adding to this the equation corresponding to (4), we get, as before,

$$\tfrac{1}{2}\int_0^{\infty} x^{q-1}[f(x)-f(-x)]\,dx = \sum_{n=1}^{\infty} b_n \int_0^{\infty} x^{q-1}\sin nx\,dx = \sum_{n=1}^{\infty} b_n n^{-q}\int_0^{\infty} x^{q-1}\sin x\,dx.$$

$$= \cos\tfrac{1}{2}q\pi\,\Gamma(q)\sum_{n=1}^{\infty} n^{-q}b_n. \tag{II}$$

Again in like manner,

$$\int_0^1 \frac{f_1(x)-C}{\sin x}\cdot x^{q-1}\sin x\,dx = \sum_{n=1}^{\infty} B_n\int_0^1 x^{q-1}\sin x\sin nx\,dx, \tag{1}$$

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where $$B_n = \frac{1}{\pi}\int_{-\pi}^{\pi} (f_1(x) - C)\operatorname{cosec} x \sin nx\, dx,$$

and therefore

$$B_{n+1} - B_{n-1} = 2a_n, \qquad B_2 = 2a_1, \qquad B_1 = -2C. \tag{2}$$

Hence the summation on the right-hand side of the equation (1), just written down, is the unique limit when m increases indefinitely of one half of the following expression :—

$$\begin{aligned}\sum_{n=1}^{n=m} 2B_n \int_0^1 x^{q-1}[\cos(n-1)x - \cos(n+1)x]\,dx &= B_1\int_0^1 x^{q-1}\,dx + B_2\int_0^1 x^{q-1}\cos x\,dx \\ &\quad - B_{m-1}\int_0^1 x^{q-1}\cos mx\,dx - B_m\int_0^1 x^{q-1}\cos(m+1)x\,dx \\ &\quad + \sum_{n=1}^{n=m-1} x^{q-1}(B_{n+1} - B_{n-1})\cos nx\,dx. \end{aligned} \tag{3}$$

Hence, using (2), we get from (1) the following equation :—

$$\int_0^1 x^{q-1} f_1(x)\,dx = \sum_{n=1}^{\infty} a_n \int_0^1 x^{q-1}\cos nx\,dx,$$

since the second and third terms on the right-hand side of (3) have, as m increases indefinitely, the unique limit zero, B_m and B_{m-1} being the Fourier coefficients of a summable function.

But, by the usual argument,

$$\int_1^{\infty} x^{q-1} f_1(x)\,dx = \sum_{n=1}^{\infty} a_n \int_1^{\infty} x^{q-1}\cos nx\,dx.$$

Adding the last two equations, we get, as in § 3, the required result :—

$$\int_0^{\infty} x^{q-1} f_1(x)\,dx = \cos\tfrac{1}{2}q\pi\,\Gamma(q)\sum_{n=1}^{\infty} n^{-q}a_n. \tag{II}$$

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The Charges on Ions in Gases, and Some Effects that Influence the Motion of Negative Ions.

By Prof. JOHN S. TOWNSEND, F.R.S.

(Received December 12, 1910,—Read January 12, 1911.)

1. In two previous papers published in the 'Proceedings of the Royal Society,'* a method was described of finding directly the charges on positive and negative ions produced by secondary Röntgen rays in gases, in terms of the charge on a monovalent ion in a liquid electrolyte; and the results of some experiments made with air were given.

A number of investigations have since been made with oxygen, hydrogen, and carbonic acid, which have taken a considerable time to complete, for although a determination of the charge can be made very accurately from a few simple observations, it requires a long time to investigate the effect produced by complete drying on the motion of the negative ions. This effect can be observed by means of the same kind of experiments as are necessary for determining the charges on the ions, and it is of considerable interest to find at what forces and pressures the negative ions in dry gases assume the corpuscular state and move under an electric force according to laws that are quite different from those which govern the motions of the positive ions.

In all these experiments exactly similar results were obtained with the three gases that have been examined, as were previously obtained with air.

With regard to the charges on the negative ions, the values obtained for the product Ne (N being the number of molecules per cubic centimetre in a gas at 760 mm. pressure and 16° C., and e the charge on an ion in electrostatic units) with different forces, pressures, and strengths of radiation were all practically the same and nearly equal to $1{\cdot}22 \times 10^{10}$, which is the value of Ne for monovalent ions in liquid electrolytes. The mean values of Ne obtained in a set of experiments were $1{\cdot}23 \times 10^{10}$, $1{\cdot}24 \times 10^{10}$, $1{\cdot}23 \times 10^{10}$, for oxygen, hydrogen, and carbonic acid respectively.

The values of Ne for positive ions, under different conditions of force and pressure, were nearly the same as for negative ions when the secondary rays ionising the gas proceed from a bright metallic surface, the corresponding numbers being $1{\cdot}24 \times 10^{10}$, $1{\cdot}26 \times 10^{10}$, and $1{\cdot}32 \times 10^{10}$. Higher values of Ne were obtained for positive ions in all gases when the rays proceeded from a surface covered with a thin layer of vaseline, showing that some of the positive ions produced by the more penetrating radiation have double

* 1908, A, vols. 80 and 81.

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charges. The mean values obtained for the three gases under these conditions are $1{\cdot}71 \times 10^{10}$, $1{\cdot}84 \times 10^{10}$, and $1{\cdot}55 \times 10^{10}$.

2. The principle that was used in these investigations was to allow a stream of ions to pass through a circular aperture in a thin plate, and after passing along a certain distance under the action of a known electric force X, to receive the ions on a disc of the same diameter as the aperture and on a flat ring surrounding the disc. The stream opens out as the ions move under the electric force, and according to the ordinary laws of diffusion the ratio R of the charge received by the disc to that received by the surrounding ring depends only on the product NeX. There is therefore a definite relation between R and X which is independent of the pressure when the motion of the ions obeys the simple laws of diffusion, as is always the case with the positive ions with the pressures and forces used in these experiments; so that the value of Ne can easily be obtained.

In finding the values of Ne for negative ions it is convenient to have a slight amount of water vapour in the gas (1/10th of a millimetre pressure is sufficient when dealing with oxygen at 10 mm. pressure, or with hydrogen at 30 mm. pressure), as the negative ions then obey the simple laws of diffusion under which their kinetic energy of agitation (or the partial pressure of the ions) is equal to that of an equal number of molecules of the gas in which they move. The determinations of Ne may also be made in perfectly dry gases at somewhat higher pressures when forces not exceeding 1 volt per centimetre are used.

3. When a gas has been dried for several days and the pressure is below a certain value, depending on X/P, a large increase in the lateral diffusion of the stream of negative ions is obtained, and only a small proportion of the ions is received on the disc on which the centre of the stream impinges. With a given force, the pressure at which this effect can be observed is greater in hydrogen than in oxygen, and is much smaller in carbonic acid than in the other gases. When this stage is arrived at the ratio R no longer follows the ordinary laws of diffusion. If the force is kept constant the opening out of the stream increases rapidly (R diminishes) as the pressure of the gas is diminished, which is in marked contrast to the effects obtained when a little water vapour is present, as the value of R is then independent of the pressure of the gas P. Thus, in dry oxygen, with a force of 2 volts per centimetre, the ratio of the charges R was found to be 0·465 when the pressure was 10 mm., and 0·27 when the pressure was 5 mm.; whereas, if a small amount of water vapour were present, both these ratios would be about 0·57.

As has already been mentioned in one of the previous papers, the motion

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of the negative ions in a dry gas at low pressure can be explained on the supposition that the negative ions have assumed the corpuscular state when the value of X/P is sufficiently great, and the relative high velocity in directions perpendicular to the direction of the electric force is due to an increase of the velocity of agitation above the average value this velocity would assume if the ions were in thermal equilibrium with the molecules of the gas.

From the experiments which have been made, it is easy to deduce the ratio of the partial pressure of the ions when diffusing in this way to the partial pressure of an equal number of molecules in thermal equilibrium with the gas, and the curves obtained for air show that when X = 1 volt per centimetre and P = 10 mm., the partial pressure of the ions is twice that of an equal number of molecules.* Since the partial pressure is proportional to mv^2, this result shows that the velocity of agitation v of the ions is greater by the factor $\sqrt{2}$ than the velocity of agitation of particles of the same mass in thermal equilibrium with the molecules of the gas.

The conclusion to which these experiments lead indicates that the velocities due to electric forces of negative ions in dry gases should be very large when the values of X/P are of the same order as those used in the above experiments.

4. Mr. R. T. Lattey† has recently investigated the velocities under these conditions, and he has found that in dry air large increases in the velocity of negative ions are obtained by making comparatively small increases in the electric force. Thus, in air at 10 mm. pressure, the velocity due to a force of 0·5 volt per centimetre is 173 cm. per second, and when the force is increased to 0·9 volt per centimetre, the velocity is 1845 cm. per second.

It is interesting to apply the theory of diffusion to calculate the coefficient of diffusion of negative ions into air under the above conditions, as the investigation shows how the group of molecules associated with each ion diminishes as the force increases. This method was used some time ago‡ to find the masses of negative ions in gases at atmospheric pressure when acted on by small forces. When X/P is small, then, the apparent mass of an ion in air is constant over a large range of values of X/P. The rate of diffusion of the ions is slow in this case, and, by comparing the rate of diffusion of ions into air with that of CO_2 into air, it may be seen that the apparent mass of the ion is about 11 times as great as that of a molecule of carbonic acid.

In applying the theory of diffusion to the cases in which X/P is large, it is

* J. S. Townsend, 'Roy. Soc. Proc.,' 1908, vol. 81, p. 468.
† R. T. Lattey, 'Roy. Soc. Proc.,' 1910, A, vol. 84.
‡ J. S. Townsend, 'Phil. Trans.,' 1899, A, vol. 193.

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necessary to give the correct value to the partial pressure p of the ions, since the velocity under the electric force and the rate of diffusion both depend on the velocity of agitation of the ions.

The equations of motion of the ions are of the form

$$\frac{1}{K}(pu) = -\frac{dp}{dx} + nXe,$$

so that the velocity u under the force X is given by the equation

$$\frac{1}{K}(pu) = nXe,$$

K being the coefficient of diffusion while the force is acting.

Usually, as when X/P is small, the partial pressure p of the ions is connected with the number of ions per c.c., n, by the equation $p/n = \Pi/N$, N being the number of molecules per cubic centimetre of a gas at atmospheric pressure Π and temperature 16° C., which is the temperature of the gas when the velocity u was determined. When $X = 0{\cdot}9$ volt per centimetre and $P = 10$ mm., the partial pressure p is larger than the above value by the factor 1·85, so that on substituting for p its value in terms of n the equation for K becomes

$$K = \frac{1{\cdot}85 \times \Pi u}{NeX} = 93,$$

since $u = 1845$, $X = 0{\cdot}9/300$ and $Ne = 1{\cdot}22 \times 10^{10}$.

The high value thus obtained for K is due partly to the fact that the velocity of agitation of the ions exceeds that of particles of equal mass in thermal equilibrium with the gas by the factor $\sqrt{1{\cdot}85}$. Hence particles of* equal mass would, under ordinary conditions, diffuse into air at 10 cm. pressure at a rate corresponding to the value of K, $93/\sqrt{1{\cdot}85} = 71$. The coefficient of diffusion of CO_2 into air is 1·42, the sum of the pressures of the gases being 760 mm., so that at 10 cm. pressure the coefficient of interdiffusion would be 10·8. Experiments on diffusion show that the coefficients of interdiffusion are inversely proportional to $\sqrt{m_1 m_2}$, m_1 and m_2 being the masses of the molecules of the two gases. Hence the ratio of the mass M of the negative ion to the mass m of a molecule of CO_2 is $M/m = (10{\cdot}8)^2/(71)^2 = 1/43$. The quantity M is the average value of the mass of the group of molecules associated with the ion, which is continually changing, and the above investigation shows that the average value must be less than the mass of a molecule of air when $X/P = 0{\cdot}09$. This shows that during part of the

* Since the rates of diffusion of different gases into a standard gas are approximately proportional to the velocities of agitation of the molecules of the different gases, it is assumed here that the rates of diffusion of the ions are also proportional to their velocities of agitation.

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time the negative electron must be free from molecules of the gas. When X/P increases, M becomes smaller still, but as the velocities have not yet been determined accurately for higher values of X/P, further investigation on these lines must be postponed.

In order that the equations of diffusion should hold in these cases, it is necessary that the velocity of the ion in the direction of the electromotive force should be small compared with the velocity of agitation. It is easy to show that this condition holds. Since the velocity of agitation of a molecule of CO_2 at 0° centigrade is 4×10^4 centimetres per second, the velocity of particles of an average mass 1/43 of that of the molecules of CO_2 would be $2{\cdot}8 \times 10^5$, and while under the electric force their velocity of agitation would be $2{\cdot}8 \times 10^5 \times \sqrt{1{\cdot}85} = 3{\cdot}8 \times 10^5$, which is large compared with the velocity, 1845 centimetres per second, in the direction of the electric force.

On the Energy and Distribution of Scattered Röntgen Radiation.

By J. A. Crowther, M.A., Fellow of St. John's College, Cambridge.

(Communicated by Prof. Sir J. J. Thomson, F.R.S. Received December 13, 1910,—Read January 26, 1911.)

Introduction.

It has been shown by Prof. Sir J. J. Thomson that it is possible, on certain assumptions, to calculate the number of electrons in an atom of any element from considerations of the scattering undergone by a rapidly moving electrified particle in the substance. In a paper recently read before this Society* I was able, by means of experiments there described, to show that the scattering of homogeneous β-rays by thin sheets of different substances did follow very closely the laws predicted by the theory, and to calculate the number of electrons contained in the atoms of some half dozen different elements. It was found that, in every case, the number of electrons per atom was equal to about three times the atomic weight.

Although the agreement between theory and experiment was very close, it seemed desirable to collect as much independent evidence as possible upon such a point. Some years ago Prof. Sir J. J. Thomson† showed that in the phenomenon of the scattering of a beam of Röntgen rays we have another possible method of attacking the problem.

* 'Roy. Soc. Proc.,' 1910, A, vol. 84, p. 226.

† 'Conduction through Gases,' 1906, p. 321.

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Assuming that the scattered Röntgen radiation is emitted by the electrons in the atoms traversed by the primary rays executing forced vibrations in the period of the incident rays, it can easily be shown that the energy radiated per electron is equal to

$$\frac{8\pi}{3}\frac{e^4}{m^2} \cdot E,$$

where E is the energy in the primary pulse, and e and m the charge and mass of the electron. The total energy radiated by a given mass of substance is therefore equal to

$$\frac{8\pi}{3} N \frac{e^4}{m^2} \cdot E,$$

where N is the total number of electrons in the given mass. This equation gives us an independent method of arriving at the number of electrons in the atom.

So far as I am aware, no determinations of the energy of scattered Röntgen radiation have been made since the early experiments of Barkla* on the secondary radiation from gases. He compared the ionisation in two similar electroscopes, one placed in the path of the primary rays, the other in a direction at right angles to it. He thus compared the energy of the secondary rays in a given fixed direction with that of the incident beam. To deduce the total secondary radiation he assumed a law of distribution deduced from the simple theory described above. As no experimental proof of this law of distribution had been given, and in view of the new light which has been thrown upon the whole subject since these early experiments were performed, it was thought desirable that a fresh determination of the energy of the scattered Röntgen radiation should be made.

It was not found feasible to measure immediately the whole of the rays scattered by a given radiator. The experiment therefore resolved itself into two parts:—

(1) The comparison of the intensity of the scattered radiation from a given radiator in a fixed plane (namely, that at right angles to the primary beam).

(2) The determination of the distribution of the scattered radiation around the radiator.

The following sections of this paper describe the methods employed and the results obtained.

* Barkla, 'Phil. Mag.,' 1904, [6], vol. 7, p. 543.

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On the Energy of the Röntgen Radiation Scattered in a Plane at Right Angles to the Primary Beam.

The direct mechanical measurement of the energy of Röntgen radiation is practically impossible. In order to compare the intensities of two given streams of Röntgen radiation, we must rely on their power either to affect a photographic plate or to ionise a gas. Of the two methods, the latter is the more definite, and the less open to objection. In fact, if the two beams have the same penetrating power, and pass through the ionisation chambers without striking any solid object, it seems reasonably certain that the amount of ionisation produced per unit length of path in the chamber will be simply proportional to the energy of beams.

If, however, the rays fall upon the electrodes and walls of the ionisation chamber, the bulk of the ionisation produced is due to the emission of corpuscular radiation from the substances struck. The amount of this will depend upon the shape and material of the chamber, and the way in which the rays strike it. Results with two different chambers will therefore not in general be strictly comparable. This objection, however, does not apply if the *same* ionisation chamber is used to measure successively different quantities of radiation, providing all pass through the chamber in the same way.

As it was desirable, on account of possible variations in the X-ray tube, to make simultaneous measurements of the primary and scattered radiations, and to eliminate as many sources of uncertainty as possible, it was decided to arrange matters so that neither the primary nor the secondary rays should impinge on any solid object in the vicinity of the ionisation chambers. The effect to be measured was thus greatly reduced, but it was thought that this was more than compensated for by the increased certainty that the measurements of the two beams were really comparable.

The methods employed will be readily understood from fig. 1, which represents a section of the apparatus. The X-ray tube F supplying the rays is completely enclosed in a thick lead box, to eliminate any fear of stray radiations; the leads from the coil were introduced through thick porcelain tubes. A narrow pencil of rays, limited by a series of circular apertures A, A, passes upwards through the lead tubes T, T, so that no radiation can emerge into the secondary ionisation chamber except at the point R, where a gap 2·5 cm. in length is left for the radiator. On its way, the beam passes through the small primary ionisation chamber P, fitted with two parallel aluminium electrodes e, e', well out of the path of the rays. The measuring electrode e is provided with a guard ring in order to ensure a uniform field across the chamber.

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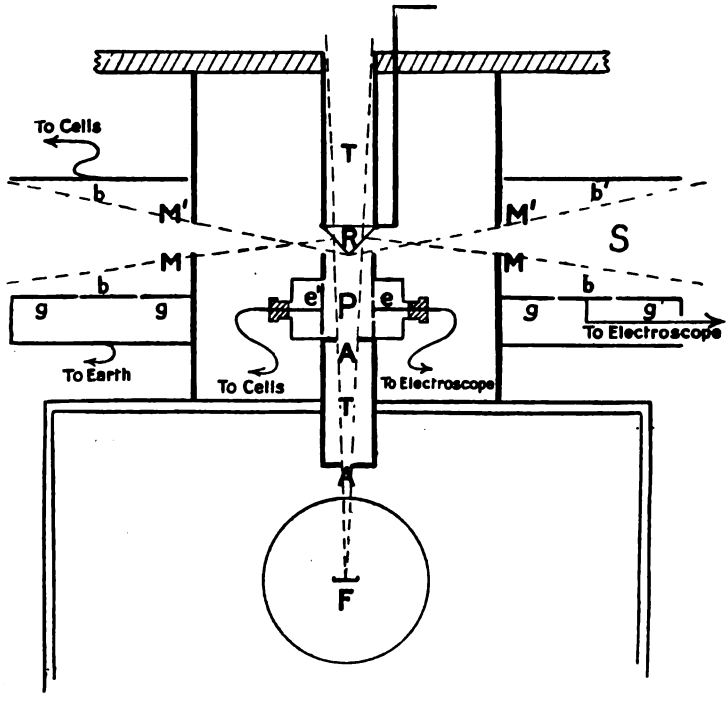

FIG. 1.

The rest of the apparatus is symmetrical about the line of the primary beam, which it completely surrounds like a belt. MM and M'M' are two lead cylinders, 24 cm. in diameter and 2·5 cm. apart, and serve to limit the secondary rays from R to a fairly narrow sheet. The secondary ionisation chamber S is fitted with two parallel plate electrodes b, b'; the measuring electrode b being surrounded by guard rings g, g, as in the case of the primary chamber P. Wires passing through earthed tubes, not shown in the diagram, connect the electrodes b and e to two Wilson electroscopes; b' and e' are charged to saturation potentials from a cabinet of accumulators.

The radiator R took the form of a hollow cone of aluminium foil, with a vertical angle of 90°. The primary rays thus met it everywhere at an angle of 45°, and the secondary rays emerged at the same angle. The scattered radiation from the air was not sufficient to measure with any accuracy.

As the chamber S was large, there was a very appreciable spontaneous ionisation current across it. To eliminate this, a cylindrical ionisation chamber, charged to the opposite potential, was connected to the same electroscope. The effective volume of this compensator could be varied by

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means of an earthed tube sliding over the inner electrode. By varying the length of the electrode exposed, the two currents could be made to neutralise each other.

In making the measurements, readings were taken with the rays passing, but with no radiator at R, and then with the radiator in position. The difference gave the effect due to the radiator alone. The effect in the absence of the radiator was always very small.

By means of a key, not shown in the figure, the electrode b could be directly connected to the electrode e of the primary chamber. In this way the capacities of the two systems could be directly compared.

To compare the relative amounts of energy in the primary and secondary beams, we may proceed as follows:—

Let E_P be the energy per unit volume in the primary beam,
α_P its cross-section, and
d_P the effective length of path in the ionisation chamber; that is to say, the length of path in that portion of the gas of which the ionisation is measured.

The volume of gas ionised is thus, $\alpha_P d_P$, and the rate of ionisation is therefore $kE_P\alpha_P d_P$, where k is a constant depending on the nature of the gas and the hardness of the rays. Similarly, for the secondary beam, we have the rate of ionisation equal to $kE_S\alpha_S d_S$, where k is the same factor as before, since the secondary rays are of the same hardness as the primary.

If q is the number of ions of one sign produced in a time t, the charge conveyed to the electrode in that time is equal to qe, where e is the charge on an electron. If the capacity of the electrode is c, and the potential acquired in the time t is equal to v, we have $qe = cv$, thus the rate of production of ions $= q/t = cv/et$.

Equating these expressions, we have

$$kE_S\alpha_S d_S = \frac{c_S v_S}{et}, \qquad kE_P\alpha_P d_P = \frac{c_P v_P}{et}$$

so that

$$\frac{E_S\alpha_S}{E_P\alpha_P} = \frac{v_S}{v_P} \cdot \frac{c_S}{c_P} \cdot \frac{d_P}{d_S}.$$

Since for a limited beam the energy crossing any cross-section of the beam in a given time is constant, $E\alpha$ is constant for a given beam of radiation.

The following are the experimental values:—

$$d_P = 1{\cdot}0 \text{ cm.}, \qquad d_S = 5{\cdot}0 \text{ cm.}, \qquad c_S/c_P = 1{\cdot}33.$$

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Rate of charging up of the two systems in volts per minute :—

v_S.	v_P.	v_S/v_P.
0·074	12·0	0·0062
0·070	11·2	0·0063
0·068	10·5	0·0065
0·068	11·0	0·0062
0·069	11·2	0·0062
0·078	12·2	0·0064
	Mean value.....	0·0063

Thus $$\frac{E_S\alpha_S}{E_P\alpha_P} = \frac{v_S}{v_P} \cdot \frac{c_S}{c_P} \cdot \frac{d_P}{d_S} = 0{\cdot}0063 \times 1{\cdot}33 \times \tfrac{1}{6} = 0{\cdot}00168.$$

The thickness of the aluminium radiator measured along the path of the primary rays was 0·109 mm. The angle of emergence of the secondary beam was 6° 24′ on each side of a plane through the radiator perpendicular to the primary beam.

The value given above has still to be corrected for the absorption of the primary and secondary rays in the radiator itself. Although the conical radiator was quite symmetrical about the primary beam, the equations obtained for the absorption in the radiator were not capable of explicit evaluation. The radiator was purposely made as thin as possible, in order to make the correction as small as possible. The following method was adopted for its determination: Consider the cross-section of the cone made by any plane perpendicular to its axis, and therefore to the primary beam. This cross-section will take the form of a ring, bounded by two concentric circles, whose distance apart is equal to $t\sqrt{2}$, where t is the thickness of the foil of which the cone is made. Consider any point P in this ring whose distance from the outer circle is y. Then the distance traversed by the primary rays in the cone in reaching P is also y, since the cone is inclined to both primary and secondary rays at an angle of 45°. The intensity of the primary rays at P is therefore $I_0e^{-\lambda y}$, where λ is the coefficient of absorption of the rays. For the rays used in these experiments, λ was equal to 11·0 cm.$^{-1}$.

Consider now the secondary rays from P in the plane of cross-section. When t is very small compared to the radius of either bounding circle, the ordinate through P at right angles to the radius becomes infinitely great compared to t. In the limit, therefore, the absorption is the same as if the radiator consisted of two parallel plates perpendicular to the radius through P. In practice the absorption must always be less than this limiting value.

If y is the depth of the point P below the surface of one of the plates, the path of a ray inclined at an angle θ to the normal is $y \sec \theta$.

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If the initial intensity of radiation from P between the directions θ and $\theta+d\theta$ is $I\,d\theta$, the emergent intensity is $I\,d\theta\,e^{-\lambda y \sec\theta}$. The total emergent radiation is therefore $I\int_0^{\frac{1}{2}\pi} e^{-\lambda y \sec\theta}d\theta$ for the rays emerging on the side nearest y. For those which pass through both plates the path is $(2t\sqrt{2}-y)\sec\theta$, and the emergent radiation is therefore $I\int_0^{\frac{1}{2}\pi} e^{-\lambda(2t\sqrt{2}-y)\sec\theta}d\theta$. I have not been able to evaluate these integrals explicitly. They lend themselves, however, quite readily to evaluation by graphical methods. By actually plotting the graphs of $e^{-\lambda y \sec\theta}$ against θ for different values of y from $y=0$ to $y=0{\cdot}0109$ cm., and measuring the areas of the curves so obtained, a series of values were found for the absorption of the secondary rays, starting from different depths y in the plate. It has been shown that the absorption of the primary rays reaching a point P at a depth y in the radiator is $e^{-\lambda y}$.

Multiplying each of the values for the absorption of the secondary rays by the corresponding values of $e^{-\lambda y}$, we obtain, by a final graphical integration, the whole absorption of the rays in the material. It was found to be given by the equation

$$I/I_0 = 0{\cdot}78.$$

This represents the maximum absorption when the radius of the cross-section is large compared with the thickness of the foil. Turning now to the apex of the cone, where the cross-section is a circle of radius $t\sqrt{2}$, we can, by pursuing a similar course of operations, find the absorption for the cross-section of this shape. In this way it was found that the absorption for this case was given by

$$I/I_0 = 0{\cdot}84.$$

This represents the minimum absorption. The actual value must lie between these two. The values are not very far apart. We shall not commit any serious error if we take the true absorption in the radiator as being given by

$$I/I_0 = 0{\cdot}81.$$

I is the radiation as measured by the secondary chamber. To obtain the true value I_0, in the absence of any absorption in the radiator, we must multiply our result by $1/0{\cdot}81$, that is by $1{\cdot}24$. Making this correction, we get finally

$$E_S\alpha_S/E_P\alpha_P = 0{\cdot}00208.$$

Considering the beams at the point where their cross-section is unity, we have

$$E_S/E_P = 0{\cdot}00208.$$

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On the Distribution of the Scattered Radiation round the Radiator.

In order to measure the distribution of the rays round the radiator it was necessary to design an ionisation chamber which could rapidly and accurately be brought to any desired position with respect to the primary beam and the radiator. At the same time, as a Wilson electroscope is very sensitive to slight changes of level, and other variations in external conditions, it was necessary, if accurate measurements were to be made, that the electroscope itself should remain fixed on a firm basis. The apparatus finally designed for the experiment is shown in fig. 2.

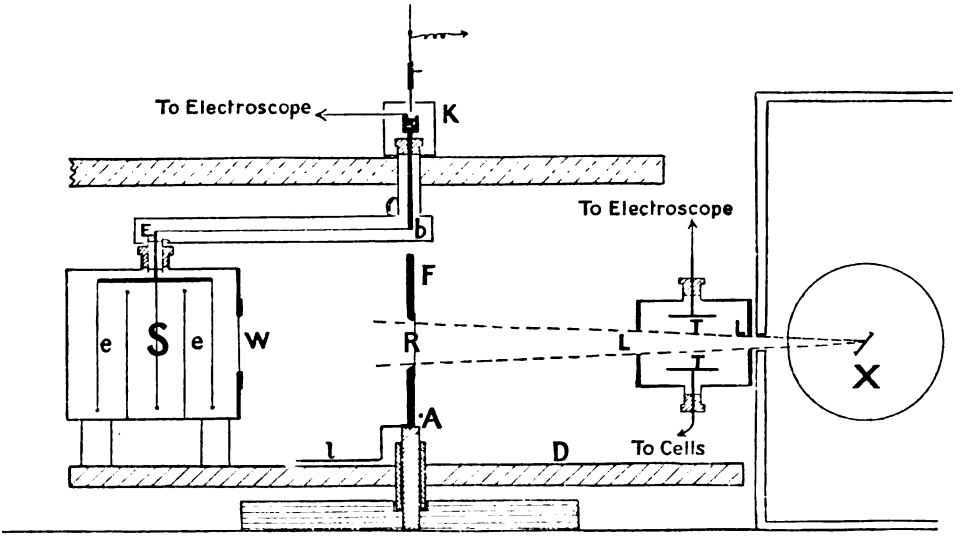

Fig. 2.

The ionisation chamber S used to measure the emergent scattered radiation is mounted upon the circumference of a large mahogany wheel D, which can be rotated about a fixed vertical axle A. The ionisation chamber S is cylindrical in shape, the cylinder being placed with its axis passing normally through the axis of rotation of the wheel. A window W, closed with thin aluminium foil, serves to admit a cone of the secondary rays of fixed angle (15°) into the ionisation chamber. A lead plate F, pierced with a suitable aperture to allow of the passage of the primary beam, is fixed to A, and serves to support the radiator R. In this way, by simply turning the wheel D, the secondary chamber S can be made to take up any position with respect to the radiator. The position of S can be read off on a circular scale fixed to D, and read by a pointer *l* attached to the fixed axle A.

As the amount of scattered radiation is very small, the ionisation

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chamber S was made fairly large, and in order to obtain saturation with a reasonably small voltage a system of plane parallel electrodes of aluminium leaf mounted on wire rings was introduced, as shown in the figure, instead of the more usual, but unsatisfactory, central wire electrode.

In order to make connection between the moving electrode E and the fixed electroscope, the key K was mounted so that the brass rod *b* came directly above the axis of rotation of the wheel D. The distance from E to *b* thus remains constant when the wheel is rotated, and the two can be joined together by a thin copper wire, shielded in an earthed metal tube in the usual way.

The focus tube X is enclosed as before in a lead box. A system of lead stops L, L, limits the emergent rays so that the cross-section of the beam at R is 3 cm. in diameter. This was verified by placing a fluorescent screen at R, when it was found that the beam passed through the aperture and was quite well defined. The primary beam passes between two parallel electrodes T, T, the ionisation between which can be measured in the usual way and serves to standardise the primary beam.

In making the measurements readings were made, as before, with and without the radiator R in position. The difference gave the true effect due to the radiator alone. Owing to the scattering of the rays in the air there was always a small but appreciable effect even when the radiator R was not present; but this was eliminated by the method of measurement described.

The radiator took the form of a sheet of the substance under experiment, the thickness being kept as small as possible, in order that the absorption of the rays in the radiator should be small. The absorption of the rays used by the substance was, however, always measured, and a correction calculated for every position of the ionisation chamber.

The following table contains a typical set of observations for an aluminium radiator. The first column of figures gives the angle θ made by the axis of S with the direction of the primary beam. R.H. and L.H. signify that the chamber is to the right or left hand, looking along the direction of the primary beam: "returned" denotes that the radiation is measured on the side of the radiator facing the incident rays; "transmitted" that it is measured on the further side. The second and third columns give the ionisation with and without the radiator, in arbitrary units, corrected for variations in the intensity of the primary beam. The fourth column is the difference of the second and third and gives the effect due to the radiator alone. The fifth column gives the correcting factor for the absorption of primary and secondary rays in the radiator. This has been calculated as follows:—Consider a small volume of

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unit area and thickness dx situated at a distance x from the front face of the radiator, which is struck normally by the primary beam. If I_0 is the initial intensity of the primary beam, the intensity on reaching the small volume is equal to $I_0 e^{-\lambda x}$, where λ is the coefficient of absorption of the rays. Suppose now that the fraction $k.dx$ of this energy is scattered in a cone of small angle about the angle θ with the normal. The path of these rays before emerging from the face of the radiator for the returned radiation is $x \sec \theta$. and for the forward radiation $(a-x) \sec \theta$, where a is the thickness of the radiator. The energy of radiation emerging from a small volume at depth x is thus $kI_0 e^{-\lambda x} e^{-\lambda x \sec \theta} dx$ in a return direction, and $k' I_0 e^{-\lambda x} e^{-\lambda (a-x) \sec \theta} dx$ in a forward direction:—

	θ.	Ionisation.		Ionisation due to radiator.	Correction factor for absorption.	I_θ.	$I_\theta \sin \theta$.
		With radiator.	Without radiator.				
	°						
R.H. "returned" ...	35	3·38	1·08	2·30	1·42	3·26	1·87
	50	2·95	0·90	2·05	1·50	3·06	2·34
	70	2·26	0·88	1·38	1·80	2·48	2·30
R.H. "transmitted"	25	11·10	3·63	7·47	1·40	10·50	4·45
	40	5·20	1·82	3·38	1·46	4·93	3·17
	60	3·54	1·54	2·00	1·67	3·34	2·90
L.H. "transmitted"	30	8·95	2·00	6·95	1·42	9·88	4·94
	50	4·10	1·03	3·07	1·55	4·76	3·65
	70	2·38	0·88	1·50	1·92	2·88	2·70
L.H. "returned" ...	35	3·25	0·90	2·35	1·42	3·34	1·91
	50	2·20	0·85	1·85	1·50	2·78	2·14
	70	2·70	0·90	1·30	1·80	2·36	2·22

The whole intensity in the direction θ is thus given by

$$I_0 k \int_0^a e^{-\lambda x (1+\sec\theta)} dx \quad \text{and} \quad I_0 k' \int_0^a e^{-\lambda [x+(a-x)\sec\theta]} dx.$$

The intensity in the same directions in the absence of any absorption is simply $kI_0 a$ and $k'I_0 a$ respectively. Evaluating the integrals, we find if I_θ, I'_θ represent the corrected and the measured values of the intensity in the direction θ,

$$\frac{I_\theta}{I'_\theta} = \frac{a\lambda(1+\sec\theta)}{1-e^{-\lambda a(1+\sec\theta)}} \quad \text{for the returned radiation,}$$

and

$$\frac{I_\theta}{I'_\theta} = \frac{a\lambda(\sec\theta-1)}{e^{-\lambda a}-e^{-\lambda a \sec\theta}} \quad \text{for the transmitted radiation.}$$

For the rays used λ was 11·0 cm.$^{-1}$.

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The values of these expressions for the different values of θ are the correction factors given in the table in column 5. The sixth column gives the values of I_θ, the intensity of the scattered radiation in the direction θ; that is to say, the energy of the scattered radiation per unit area at an angle θ with the primary beam.

According to the simple theory of scattering outlined above, the distribution of the scattered radiation should be symmetrical both about the direction of the primary beam, and about a plane perpendicular to this direction. The intensity should be a minimum in this plane, and rise to a maximum on both sides of the radiator in the direction of the incident beam. The ratio of the maximum to the minimum intensities, assuming that the electrons are displaced in the plane of the wave-front, should be 2 to 1.

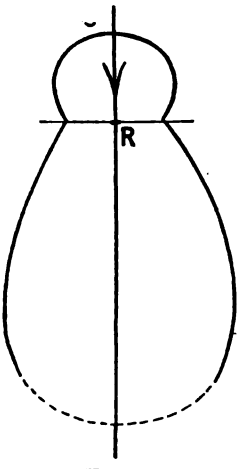

FIG. 3.

The actual distribution obtained differed considerably from this. Fig. 3 shows graphically the actual distribution around a small radiator R, the primary rays falling upon R in the direction of the arrow. Radii are drawn from R, showing the angle of inclination of the scattered rays with the normal, and lengths are marked off along them proportional to the intensity of radiation at that inclination. In this way we get a picture of the distribution of the rays about R. The same results are also shown as an ordinary graph in fig. 4.

It will be seen from fig. 3 that the scattered radiation is symmetrical about the incident beam,* but not about the plane perpendicular to it, through the radiator.

It will be seen at once from both figures that while the intensity of the scattered radiations is a maximum both forward and backward along the line of the primary beam, and falls to a minimum in the plane perpendicular to this direction, the distribution about this plane is by no means symmetrical. At any given inclination to the primary beam the intensity

* In these experiments the bulb was placed so that the path of the cathode rays in the bulb was perpendicular to the plane of rotation of the ionisation chamber. If the path of the cathode rays is in the plane of rotation, there is always a slight preponderance of the scattered radiation on that side of the primary beam to which the cathode rays are directed. This effect, which has been pointed out by several observers, is due to the partial polarisation of the primary rays. It was in order to eliminate any error due to this effect that the secondary chamber in the energy experiments already described was made to surround completely the primary beam.

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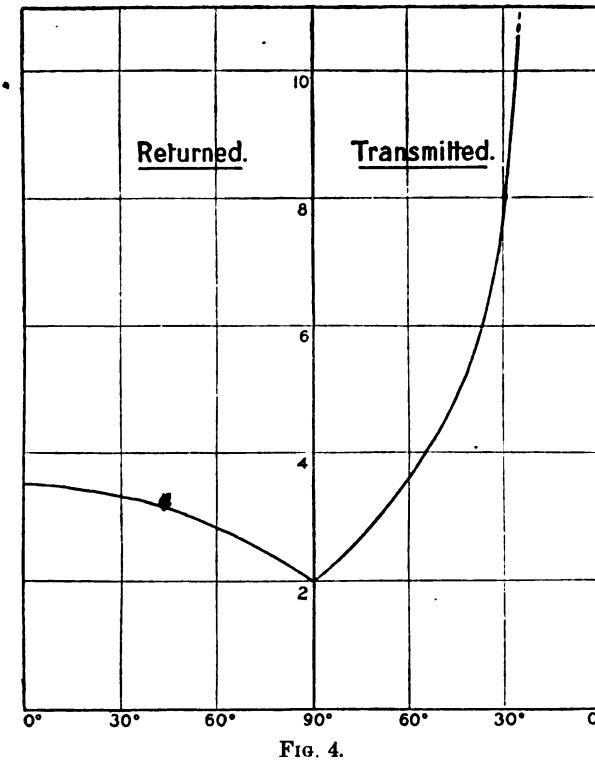

FIG. 4.

in the forward direction is always greater than that in the reverse direction, and this inequality becomes greater as the direction approaches more and more nearly to that of the primary beam. The distribution of the returned radiation agrees fairly well with that given by the simple theory. It was impossible to measure the returned radiation actually in the line of the primary beam. By interpolation, however, it was found that the intensity in this direction was about 3·64. The intensity at right angles to this was found to be 2·0; the ratio being 1·8 : 1. It seems, therefore, that while the maximum in the forward direction is greater than is required by the theory, the maximum in the reverse direction is somewhat less.

The form of curve suggested that the preponderance in the forward direction might be due to some other form of radiation superposed upon the true scattering. A considerable number of experiments have been made with a view to testing this point, but I have so far failed to obtain any evidence that such is the case. The distribution of the radiation does not seem to depend upon the thickness of the radiator, though it does to some extent upon the material, the eccentricity being rather less for paper than for aluminium. There was no appreciable difference in the hardness of the

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rays returned, and those transmitted, the relative intensities in the two directions being unaltered when sufficient aluminium was placed in front of W to cut down the radiation entering the ionisation chamber by more than one-half. The effects cannot be due to a penetrating "characteristic" radiation from the aluminium, as measurements on characteristic secondary radiation have shown that it is distributed equally at all angles round the radiator.* At present, therefore, we must regard the whole of the radiation as being purely scattered.

To obtain the whole energy of scattered radiation we may proceed as follows. Let R_θ be the intensity of the radiation at any angle θ with the primary beam, so that the energy included in a hollow cone of angle θ and increment $d\theta$ round the primary beam is equal to $R_\theta . d\theta$. The area swept out by this hollow cone on a sphere of radius r passing through the window of the ionisation chamber is $2\pi r \sin\theta . rd\theta = 2\pi r^2 \sin\theta . d\theta$. Now, if α is the area of the window, supposed to be sufficiently small to be included in this belt, the intensity of the rays I_θ entering the ionisation chamber is equal to

$$R_\theta d\theta \frac{\alpha}{2\pi r^2 \sin\theta d\theta}.$$

But α is constant, being the area of the window w, and r is constant. We can write therefore

$$R_\theta = \text{constant} \times I_\theta \sin\theta.$$

The values of $I_\theta \sin\theta$ are given in the last column of the previous table. The whole energy of the scattered radiation is equal to

$$\frac{1}{2\pi}\int_0^{2\pi} R_\theta . d\theta, \quad \text{that is to} \quad c' \int_0^{2\pi} I_\theta \sin\theta \, d\theta.$$

Similarly, the energy measured in the first part of the experiment is that included between angles of $\pm 6^\circ 24'$ with the plane perpendicular to the primary beam, *i.e.*,

$$c' \int_{\frac{1}{2}\pi - \phi}^{\frac{1}{2}\pi + \phi} I_\theta \sin\theta \, d\theta, \quad \text{where} \quad \phi = 6^\circ 24'.$$

We can integrate these quantities by a graphical method. A curve is plotted between $I_\theta \sin\theta$ and θ. The area of the whole curve gives the value of $\int_0^{2\pi} I_\theta \sin\theta \, d\theta$, that is, of the whole scattered radiation. The area included between the ordinates $\frac{1}{2}\pi \pm \phi$ gives in a similar way the energy between the angles $\frac{1}{2}\pi \pm \phi$. Drawing the curve we find that the whole area is 2292 in arbitrary units; the area between ordinates $\frac{1}{2}\pi \pm \phi$ is 138 on the same scale.

* J. A. Crowther, 'Camb. Phil. Soc. Proc.,' November, 1910.

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The energy measured in the first experiment is thus 138/2292, or 0·060 of the whole scattered radiation.

On the Energy of Scattered Radiation and the Number of Electrons in the Atom.

We are now in a position to form an estimate of the fraction of the energy of the primary Röntgen radiation scattered per unit mass of the radiator. We have found that 0·00208 of the energy of the primary beam is radiated between the angles $\pm$ 6° 24′ with the plane perpendicular to the primary beam by an aluminium radiator 0·109 mm. or 0·0109 cm. thick. We have also seen that this energy represents 0·060 of the whole scattered radiation. The total energy of scattered radiation must therefore be 0·00208/0·060 or 0·0347 of the energy in the primary beam.

The density of aluminium is 2·7; the mass per unit area of the radiator is therefore 0·0294 grammes per square centimetre. For a radiator of unit mass per square centimetre we should therefore have—

$$\frac{\text{Energy in scattered radiation}}{\text{Energy in primary radiation}} = \frac{0{\cdot}0347}{0{\cdot}0294} = \mathbf{1{\cdot}18.}$$

It must be remembered that as we have corrected our results for the absorption of the primary rays this number represents the rate at which the primary radiation is being scattered. Representing the scattering by the equation

$$dS = kI.dw.$$

where S and I are the intensities of the scattered and primary rays, and w is the mass per unit area, the number 1·18 represents the factor k, which we may term the mass coefficient of scattering.

We have seen that the elementary theory of scattering does not entirely represent the actual distribution of the scattered radiation round the radiator. It seems probable, however, that the theory is sufficiently near the truth to give us a fairly reliable estimate of the energy scattered. Assuming that this is the case, we have

$$\frac{8\pi}{3} \cdot N\frac{e^4}{m^2} = 1{\cdot}18 \text{ per grm. per sq. cm.},$$

where N is the total number of radiating electrons. Taking e as $1{\cdot}55 \times 10^{-20}$ e.m.u. (Rutherford and Geiger) and e/m as $1{\cdot}73 \times 10^{7}$ e.m.u. (Bucherer) we have

$$N = \frac{3}{8\pi} \cdot \frac{1{\cdot}18}{(1{\cdot}55 \times 10^{-20})^2 (1{\cdot}73 \times 10^{7})^2} = 1{\cdot}95 \times 10^{21} \text{ per grm.}$$

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Now the mass of a hydrogen atom is $1{\cdot}61 \times 10^{-24}$ (Rutherford and Geiger); the mass of an atom of aluminium is therefore

$$27 \times 1{\cdot}61 \times 10^{-24} = 4{\cdot}35 \times 10^{-23}$$

or the number of atoms of aluminium per gramme is

$$(4{\cdot}35 \times 10^{-23})^{-1} = 2{\cdot}30 \times 10^{22}.$$

The number of electrons N in this mass of aluminium as given by the scattering is $1{\cdot}95 \times 10^{24}$. The number of electrons per atom of aluminium is therefore found to be $\frac{1{\cdot}95 \times 10^{24}}{2{\cdot}30 \times 10^{22}}$ or **85.** The number of electrons per atom of aluminium obtained from the measurements on the scattering of homogeneous β-rays is 83.* The agreement between the two results arrived at from entirely different points of view is very satisfactory. It seems therefore that the estimate of the number of electrons in the atom as being three times the atomic weight is probably not far from the truth.

Summary.

The distribution of the scattered Röntgen radiation round a radiator has been measured. The intensity of the scattered radiation reaches a maximum on both sides of the radiator in the line of the primary beam, and falls to a minimum at right angles to this direction. At any given inclination to the primary beam there is a preponderance of radiation in the forward direction, the ratio increasing as the direction of the primary beam is approached.

The energy of the radiation scattered in a given direction has been compared with that in the primary beam. From the result so obtained, and the known distribution of the radiation, the total radiation scattered by an aluminium radiator has been determined.

It has been shown that the value obtained leads to the same result for the number of electrons in the atom as that previously calculated by the author from his experiments on the scattering of homogeneous β-rays.

In conclusion I wish once more to express my thanks to Prof. Sir J. J. Thomson for his inspiration and advice during the course of these experiments.

* J. A. Crowther, 'Roy. Soc. Proc.,' 1910, A, vol. 84, p. 239.

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The Origin of Magnetic Storms.

By Arthur Schuster, F.R.S.

(Received January 9,—Read January 26, 1911.)

1. Lord Kelvin,* in discussing the origin of magnetic storms, came to the conclusion that they could not be due to a direct solar action on account of the enormous energy which would have to be supplied by the sun. This verdict was generally accepted until recently, when the theory of a direct solar action has been revived in a form, which is assumed to be free from the objection raised, the magnetic action being supposed to be due to a swarm of electrified corpuscles ejected by the sun. The question of energy has not, so far as I know, been discussed in this case, and it seems to be taken for granted that the total energy of the magnetic field due to a swarm of corpuscles is equal to the sum of the energies of each, calculated as if the others were not present. If the corpuscles are sufficiently far apart, this is approximately correct; but in that case the magnetic field itself would have to be negligible, except within molecular distance from each particle. How far we may go wrong by treating the energy as if it could be obtained by a process of addition becomes apparent when we consider that such treatment would lead to coefficients of self-induction which are proportional to the length of a circuit and independent of its shape.

2. If A_1, A_2, A_3 represent the components of electro-kinetic potential and u_1, u_2, u_3 the current components at any point, the total electro-magnetic energy is given by

$$T = \tfrac{1}{2}\iiint (A_1u_1 + A_2u_2 + A_3u_3)\,dx\,dy\,dz.$$

In a previous paper† I have shown that in evaluating the integral the displacement currents need not be taken into account so far as they affect the components of current, while they become important, however, in the calculation of A. If we take the axis of z to be the direction of motion, the expression for the energy reduces to

$$T = \tfrac{1}{2}\iiint Au\,dx\,dy\,dz,$$

where u stands for the convection current per unit surface within the swarm of electrons and A is the component in the direction of motion of the electro-kinetic momentum due to the whole current.

* 'Roy. Soc. Proc.,' 1892, vol. 52, p. 307.

† 'Phil. Mag.,' 1897, vol. 43, p. 1.

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The correct value for A at a point x, y, z, is*

$$\iiint u\, d\xi\, d\eta\, d\zeta \left(\frac{1}{r} - \frac{1}{2}\frac{d}{dr}\frac{z-\zeta}{r}\right).$$

where u is now supposed to be a function of ξ, η, ζ. This is to be integrated over the space occupied by the swarm, which we suppose to be cylindrical. In the calculation of A we take the two terms separately. The first is identical with the gravitational potential of matter spread with density u through the space filled by the swarm of moving electrons. As the swarm has a length which is great compared with its cross-section, the calculation may be simplified by assuming the value of A to be constant in a plane at right angles to the direction of motion. In a section at a distance h from the front, the gravitational potential due to that part of the cylinder which is in front of the section is then found to be

$$\pi u \left\{ a^2 \log\left(\frac{h}{a} + \frac{\sqrt{(h^2+a^2)}}{a}\right) + h\sqrt{(h^2+a^2)} - h^2 \right\}.$$

The second part of the integral to be determined is

$$-\tfrac{1}{2}\iiint \frac{d}{dz}\left(\frac{z-\zeta}{r}\right) d\xi\, d\eta\, d\zeta = \tfrac{1}{2}u \iiint \frac{d}{d\zeta}\left(\frac{z-\eta}{r}\right) d\xi\, d\eta\, d\zeta = -\frac{h}{2}u \iint d\eta\, d\zeta.$$

If the front portion of the cylinder alone be considered, this is equal to the gravitational potential of matter spread uniformly with surface density $\frac{1}{2}hu$ over the front end of the cylinder, and is therefore equal to

$$-\pi h\,(\sqrt{(h^2+a^2)} - h)\,u.$$

The two terms together therefore give for the value of A, if α be written for h/a,

$$\pi\{a^2 u \log[\alpha + \sqrt{(1+\alpha^2)}]\}.$$

To get the electro-kinetic energy, this has to be multiplied by $\frac{1}{2}u$ and integrated over the cylinder. The parts of A due to the two portions of the cylinder contribute equally, and we have therefore

$$\begin{aligned} \mathrm{T} &= \pi^2 a^5 u^2 \int_0^\alpha \log[\alpha + \sqrt{(1+\alpha^2)}]\, d\alpha \\ &= \pi^2 a^5 u^2 \{\alpha \log[\alpha + \sqrt{(1+\alpha^2)}] + 1 - \sqrt{(1+\alpha^2)}\}, \end{aligned}$$

where α now represents the ratio of the total length of the cylinder to the radius of its cross-section. If α be large, we may write, approximately,

$$\mathrm{T} = \pi \mathrm{V} a^2 u^2 (\log 2\alpha - 1),$$

* 'Phil. Mag.,' 1891, vol. 32, p. 9.

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where V stands for the volume of the cylinder. It is useful to introduce the magnetic force at the boundary of the cylinder, which is $H = 2\pi a u$, so that

$$T = \frac{1}{4\pi} H^2 V (\log 2\alpha - 1),$$

and the energy per unit length becomes

$$T = \tfrac{1}{4} H^2 a^2 (\log 2\alpha - 1).$$

As the swarm increases in length, the energy increases in a greater proportion than the length.

3. Before discussing the results obtained, we write down the corresponding expressions for a swarm of electrons uniformly filling a sphere and moving with speed w in the direction of the axis of z. If e be the total quantity of electricity in the sphere, the magnetic energy outside the sphere is $e^2w^2/3a$.

The magnetic force inside the sphere is $e'w(x^2+y^2)^{\frac{1}{2}}/r^3$, where e' stands for the quantity of electricity contained in a sphere of radius r, which is equal to er^3/a^3. Introducing this and integrating through the volume of the sphere, we find for the total electro-kinetic energy of the moving sphere $2e^2w^2/5a$, the magnetic force at the surface in the equatorial plane being ew/a^2. If H denote this magnetic force, the energy is

$$T = \tfrac{2}{5} a^3 H^2 = \frac{3}{10\pi} H^2 V,$$

if V be the volume of the sphere.

Comparing the expressions for the cylinder with those for the sphere, it appears that in writing $H^2V/4\pi$ for the energy contained in volume V we shall underrate its value in both cases. As H is the magnetic force at the point where it reaches its greatest value, we may take the above expression to represent the smallest amount of energy which a swarm of electrified particles can contain if it occupies a volume V and causes a magnetic force H.

4. Sir Oliver Lodge* has calculated the numerical values of the dimensions of a swarm of electrons, producing a magnetic field as great as that of the storm of September 25, 1909. If the velocity of the particles be estimated at 10^9, he finds, taking into account the duration of the storm, that the square of the cross-section has the value 5×10^{20}, so that the total energy transmitted in unit time would be $4 \times 10^{28} H^2$, or, as the change in the magnetic force on this occasion was 0·004, we obtain finally $6{\cdot}4 \times 10^{23}$ ergs per second for the rate at which the sun would have to emit energy.

The number obtained by Lord Kelvin was $1{\cdot}5 \times 10^{36}$ in a storm which caused a magnetic force less than the tenth part of that considered by

* 'Nature,' 1892, vol. 52, p. 307.

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Sir Oliver Lodge. The difference is more apparent than real, because in the theory criticised by Lord Kelvin the whole surface of the sun was concerned in the emission of energy, while a swarm of electrons such as we are now considering would be projected only from a limited region. If, in the example chosen, the surface from which the swarm is ejected covered a circular patch subtending an angle of about 4′ of arc, as seen from the earth, we should have found for the work per unit surface of the sun a number identical with that given by Lord Kelvin.

5. The question arises whether, and in what way, the sun can supply the large electro-kinetic energy of the magnetic field which surrounds the swarm of electrified particles. If w and μ denote respectively the velocity and mass of each particle as it leaves the sun, the original energy of a number NV contained in volume V, is $\frac{1}{2}\mu NVw^2$, and this energy has to provide not only the magnetic field, but also the energy which the particles retain in consequence of their own mass, or rather of the electro-kinetic energy of the magnetic field which they carry with it in their immediate surroundings.

This latter part of the energy would be $\frac{1}{2}\mu NVu^2$, if u be the velocity with which they sweep past the earth. It appears therefore that u must be smaller than w, which means that the particles must lose energy between the sun and the earth. This implies a retarding force, which hitherto has been left out of account. The stream of particles moves, in fact, in a magnetic field, which is constantly increasing and thereby gives rise to an electromotive force, opposing the motion. As the stream increases in length, the electro-kinetic energy, which is due to the superposition of the magnetic fields of all the particles, soon considerably exceeds the sum of the energies of each particle taken separately, and therefore in the final stage u^2 will be small compared with w^2. In any case, we must conclude that the original energy supplied by the sun per unit volume exceeds $H^2/4\pi$.

Hence

$$2\pi\mu Nw^2 > H^2;$$

or, substituting for H the magnetic force at the cylindrical boundary,

$$w^2/u > Hac/\mu.$$

Substituting for H and a the numerical values given by Sir Oliver Lodge, we find

$$w^2/u > 10^{15}.$$

It follows that, even though we may estimate the original velocity as nearly equal to that of light (provided μ is not materially increased), the velocity of the particles as they sweep past the earth is reduced to about nine kilometres a second. The passage between the sun and earth would take

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about a year, so that the main purpose for which the hypothesis was framed, which was to find a connecting link between disturbances on the sun and nearly simultaneous effects on the earth, would cease to be served. The difficulty might to some extent be overcome if it were possible to reduce the cross-section of the swarm, but this was fixed to suit the duration of the storm, and could not materially be diminished. It will also appear that the electrostatic repulsion between the particles puts a small cross-section out of the range of possibility.

We may pause for a moment to consider whether more favourable results might not be obtained by assuming the projected particles to have masses comparable with those of ordinary atoms of matter. It seems, however, impossible that the high velocity required could be imparted to such heavy carriers, except by a radioactive process, and examination shows that inadmissibly large quantities of radium would have to be involved, if appreciable magnetic effects are to be produced.

6. We proceed to examine the electrostatic effects, which must show themselves in the gradual expansion of the beam and in the redistribution of the electricity on the surface of the earth. The magnetic force H at a point P due to a charge e moving with velocity u is $eu \sin\theta/r^2$, if θ be the angle which the line between P and the charge forms with the direction of motion. On the other hand the electric force at P resolved in a plane at right angles to the direction of motion is $ec^2 \sin\theta/r^2$, where c is the velocity of light. Hence if E be the component of electric force at right angles to the direction of motion,

$$\mathrm{E} = \frac{c^2}{u}\mathrm{H}.$$

This relation must hold for the total effect of all current elements, provided they are all parallel. The acceleration at P of the charge e having mass μ is

$$f = \frac{c^2 e}{u\mu}\mathrm{H}.$$

We found from energy consideration that c^2/u must be greater than 10^{15}, but leaving this out of account altogether, and putting for u its greatest possible value, which is c, we may assert that

$$f > 5{\cdot}6 \times 10^{17}\mathrm{H}.$$

With 0·004 for the value of H this would give a minimum for f which is greater than 22×10^9, an acceleration sufficient to drive a particle in the first second through a distance equal to more than 8 diameters of the earth. If it be remembered that this is the acceleration at the edge of the swarm, when it has reached the earth, and that the average acceleration between the

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sun and the earth must have been greater, we must conclude that a swarm of electrons packed with sufficient density to cause a magnetic effect would soon get dissipated laterally into space until its magnetic action becomes negligible. The electro-magnetic attraction of the particles has not been lost sight of, but it only partly neutralises the electrostatic effect when the velocity is that of light, and with all admissible velocities it is negligible. Returning to the electric force $E = c^2H/u$, consider a point on the earth's surface where its direction is vertical. The force causes an electric field which is more than doubled by the charge induced on the earth. Again substituting the lowest possible value for c^2/u ($u = c$) we find that the electric field would be at least 600H volts per centimetre or with previous value of H, 2·4 volts per centimetre. This exceeds several times the normal field of the earth, which, if the particles are negatively charged, would, on the approach of a storm, become reversed in sign and nearly doubled in intensity. No such effect is observed, but, on the contrary, one characteristic feature of atmospheric electricity is, that it remains undisturbed even by the most violent magnetic storm. If the electric force continued to act it might be argued that owing to the electric conductivity of the atmosphere the screening which would take place might explain the absence of electrostatic effects. But the small velocity of diffusion of the ions which cause the atmospheric conduction would prevent any effective screening of such sudden changes of magnetic force as are observed during magnetic storms. If the energy considerations are taken into account, the value for the electrostatic field for the same magnetic force would have to be multiplied by 100,000.*

7. The results of the previous investigation conclusively prove that magnetic storms cannot be due to a direct magnetic action of swarms of electrified particles. We must reject that theory and can do so without a pang of regret, so far as that simple variety of it is concerned, which simply considers the effect of kathode rays projected from the sun outwards, because, apart from the consideration now brought forward, the magnetic effects of such rays could not reproduce, even roughly, the characteristic features of a magnetic disturbance. It is otherwise with the more refined form in which the theory has been presented by Prof. Birkeland, who, qualitatively at any rate, has shown that an agreement might be reached, if we can imagine the particles to be drawn in towards the earth, by its magnetic forces, so that for the time being their motion is regulated by the position of the earth's magnetic poles. Nevertheless, the argument from

* The effect of a swarm of electrified particles on the earth's electric field has already been pointed out by Dr. George Simpson ('Nature,' 1909, vol. 82, p. 37).

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energy and from electrostatic considerations alike, has now been shown to be fatal to the theory in any form.

If, therefore, we wish to adhere to the hypothesis that the connexion between solar outbursts and terrestrial magnetism is due to a projection of particles by the sun, we are driven to accept the view, which I have advocated for a long time, that the particles act by increasing the ionisation of the outer regions of the atmosphere and allow the electromotive forces which are always present locally to increase the intensity of the electric circulation. The rotation of the earth, which is the primary cause of the electromotive forces which come into play, then becomes responsible for the energy.

The view that the impact of the projected particles causes luminosity remains allowable, so that Prof. Birkeland's theory of the aurora borealis is still tenable.

On the Periodicity of Sun-spots.

By Arthur Schuster, F.R.S.

(Received January 19,—Read January 26, 1911.)

In the year 1906 I presented to the Royal Society an investigation* in which it was shown that the frequency of sun-spots was subject to recurrent variations, not only in the well-known 11 years' cycle, but also in other periods, which were determined. As we now possess additional material extending over 10 years, it is interesting to examine how far the minor maxima of the subsidiary periods can be traced in the more recent records. The accompanying figure gives diagrammatically the sun-spot areas measured at Greenwich between 1898 and 1909. The numbers plotted represent the sum of the mean areas during four successive rotations, beginning with the four rotations 593/596 of Carrington's series.

There is a period of 4·79 years, which in the previous communication was shown to be persistent during the whole time covered by sun-spot records, more persistent, in fact, than that of 11 years. I have marked on the diagram the predicted times of maxima of the period with an arrow pointing upwards. The first maximum, towards the end of the year 1898, which was timed to arrive during the rotation 604, actually took place three rotations, or about $2\frac{1}{2}$ months, earlier. The second maximum (September, 1903) was

* 'Phil. Trans.,' 1906, vol. 206, p. 69.

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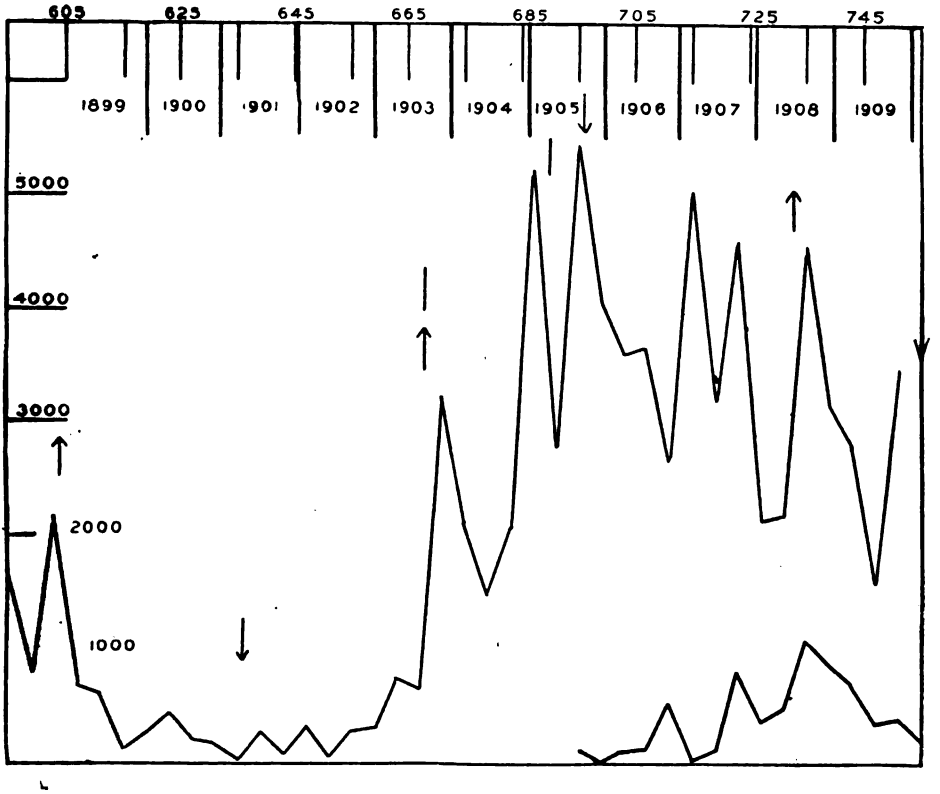
predicted to take place during rotation 668. It actually took place during the rotation 671, though an almost equally strong maximum was observed during rotation 667. We may therefore say that there is here an almost absolute coincidence in the predicted and observed times. The maximum of July, 1908, was delayed by about two months, but the activity had already risen considerably at the predicted time. In all three cases the coincidences of the predicted and actual times are very satisfactory, if it be remembered how variable is the observed maximum of the 11 years' period. This



periodicity of 4·79 years seems characterised by one or two sharp outbreaks near the time of the maximum, and throughout the time that accurate records are available it nearly always shows itself in each cycle as a separate peak in the curve representing sun-spot frequencies. The outbreaks of sun-spots connected with this period can be traced also in the magnetic records. There were several disturbances during September and October, 1898, notably one on September 9. In 1903 there was a magnetic storm on October 12, and more violent ones at the end of the month. Finally, in 1908, we had strong disturbances on September 11 and 29.

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We must conclude that the previous evidence establishing this period has been further confirmed. In the meantime the same period has been discovered quite independently in the records of magnetic declination by Mr. Oppenheim.* Taking the average daily ranges for two successive years, as observed by Lamont in Munich during the years 1836—1886, Mr. Oppenheim, using a method differing essentially from that adopted by myself and others, comes to the conclusion that it is subject to a period of 4·92 years with an amplitude of about 12 seconds of arc. The difference between 4·92 and 4·79, as found by myself, is not important, considering that Mr. Oppenheim bases his calculation on a two-year mean and only 12 complete periods. This work being apparently undertaken in ignorance of the previous discovery of this period in the sun-spot records, the moral value of the confirmation it affords, is increased.

At the foot of the diagram I have represented the average rise and fall of this period as obtained from the mean of all observations extending over a range of 16 periods. The scale is that of the larger diagram, showing that the efficiency of this outbreak has been well above the average.

A period of 4·38 years, indicated as doubtful in my previous communication, receives no support by the additional material, though the evidence is not perhaps decisively adverse. The times at which this period should have reached its maxima are marked in the diagram by arrows pointing downwards.

A further periodicity of about 8·36 years, which appeared with considerable regularity between the years 1836 and 1887, has not since then shown itself. There should have been a maximum during the summer of 1904 at a time when there actually was a considerable diminution of activity.

A few words may be said on the apparently delayed maximum of the dominant periodicity of 11 years. The date of the maximum, as deduced from Fourier's analysis, differs from that found by observation, because the analysis picks out the simple period, while the observations include the harmonics. It is known that the sun-spot curve rises much more quickly before the maximum than it falls after it. The resulting curve, when analysed, gives the simple periodicity of 11 years, with a maximum later than the observed one, and it is the first harmonic which has its maximum coinciding with the observed maximum of solar activity. The true maximum of the 11 years' Fourier period should have taken place in 1905·35, but the greatest outbreak of spots which coincide with the maximum of the 5·56 year period was to be expected already in 1903·75. The times of these maxima are indicated in the diagram by lines drawn without arrow-heads.

* 'Met. Zeits.,' 1910, vol. 27, p. 270.

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The first of them coincides with the maximum of the 4·79 period, and it is therefore open to us to ascribe this maximum to the 11 years' cycle rather than to the minor period. But in that case the subsequent behaviour of the activity becomes anomalous, as the spots ought to have diminished in number immediately afterwards. To judge from the appearance of the curve, it looks as if the two peaks in 1905 represent the true maximum of the 11 years' period, and that we must ascribe the outbreak in 1909 to some unknown cause. It was pointed out in my previous communication that the three well-established periods have periodic times which are sub-multiples of 33·375 years. It has often been remarked that the 11-year period shows particularly pronounced maxima during the first, third, and seventh decades, suggesting a periodicity of 33 years, and it is remarkable that this period can be traced in the Chinese records, reaching back to the beginning of our era.*

Though the last maximum was exceptional, in so far as it was rather below the average in intensity, the coincidence between the period of 33 years and the time of revolution of the Leonides meteorites is remarkable, and deserves careful attention. The delayed and disappointing display of Leonides at the end of last century is perhaps connected with the delayed and disappointing appearance of the last sun-spot maximum, while the exceptional brilliance of both phenomena 33 years previously is suggestive.

In the diagram the vertical scale represents sun-spot areas. Along the upper margin shorter lines are marked at intervals of 10 rotation periods, while the longer lines represent the divisions between successive years.

* 'Observatory,' 1906, vol. 29, p. 205.

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The Absorption Spectra of Lithium and Cæsium.

By Prof. P. V. Bevan, M.A., Royal Holloway College.

(Communicated by Sir J. J. Thomson, F.R.S. Received January 20,—Read March 9, 1911.)

In a paper* communicated to the Royal Society in February, 1910, I gave the results of measurements of absorption lines for the three alkali metals, potassium, rubidium, and cæsium. Up to that time I had not been able to obtain the corresponding spectrum for lithium vapour. This was owing to the fact that lithium vaporises at a considerably higher temperature than the other alkali metals, and at the high temperatures required for a sufficient density of vapour the lithium attacks the material of all tubes which I was able to use. Steel, brass, platinum, glass, silica, carbon are all attacked, and no satisfactory photographs could be obtained. Recently, however, by using a relatively large quantity of lithium in a steel tube sufficient vapour was obtained to give an absorption spectrum showing 27 lines of the principal series. The method was the same as that described in the paper referred to, with the exception that a second steel tube was placed in the outer steel absorption tube. This was simply for the protection of the outer tube, which would probably collapse after being acted on by lithium vapour at the bright red heat to which it was raised. The source of light used was the cadmium spark, as the limit of the series is so much further in the ultra-violet than in the case of the other alkali metals.

The following table gives the wave-lengths and oscillation frequencies for the complete series of lithium lines. (See Table I opposite.)

The lines 1 to 9 are given by Kayser, 10 to 27 are new.

In addition to the absorption spectrum consisting of these lines of the principal series, there is a fluted region corresponding to the similar region in the cases of sodium and potassium vapours. This extends over the wave-lengths between about 4500 and 5500, and corresponds fairly closely in position with the sodium fluted region. The fluted region is, in appearance, like those in the cases of sodium and potassium, and appears under similar circumstances—when the vapour is fairly dense, giving a broadened line for the first member of the principal series. It consists of a large number of fine lines, grouped so as to show under small dispersion bands with fairly definite edges in the central position of the spectrum—at the two ends the appearance of sharp edges is lost.

* 'Roy. Soc. Proc.,' A, vol. 83, p. 421.

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Table I.

	λ.	Possible errors.	$10^8 \lambda^{-1}$ *in vacuo*.	O−C.
1	6708·2		14902·7	
2	3232·77		30923·7	
3	2741·39		36466·4	
4	2562·60		39010·6	
5	2475·13		40389·2	
6	2425·55		41214·7	
7	2394·54		41748·5	
8	2373·9	0·2	42111·4	+0·1
9	2359·4	0·2	42370·2	+0·2
10	2348·5	0·2	42568	0
11	2340·5	0·2	42713	+0·1
12	2334·3	0·2	42827	+0·1
13	2329·0	0·3	42924	−0·3
14	2325·2	0·2	42994	−0·1
15	2321·9	0·3	43055	−0·2
16	2319·3	0·3	43103	−0·2
17	2317·1	0·2	43144	−0·1
18	2315·2	0·2	43180	−0·2
19	2313·6	0·4	43210	−0·2
20	2312·2	0·4	43236	−0·3
21	2311·1	0·2	43256	−0·1
22	2310·0	0·2	43277	−0·2
23	2309·0	0·2	43296	−0·2
24	2308·3	0·2	43309	−0·2
25	2307·5	0·2	43324	−0·2
26	2307·0	0·3	43333	−0·1
27	2306·5	0·3	43343	0

The table contains in the second column the estimated possible errors in the determinations of the wave-lengths. Hicks* has emphasised the importance of recording the possible errors in wave-length determinations, and, although these determinations do not make any pretence at great accuracy, the possible errors for each wave-length have been estimated. They vary through the series owing to the differences in the situation of lines; for example, the two lines 19 and 20 of the series have possible errors of 0·4 given to them owing to the fact that they occur close to the cadmium line of wave-length 2313, and where we have absorption lines close to an emission line of the source of light—in this case the cadmium spark—the exact position of the centre of the line is difficult to determine. An attempt was made to obtain the absorption spectrum with another source than the cadmium spark, but without success—the cadmium spark seems to give the best intensity of light so far in the ultra-violet as the lines under discussion. The lines 8 and 9 were measured again. The values given by Kayser are due to Liveing and Dewar, and no estimate of error is given. The values obtained by me are the same as those of Liveing and Dewar.

* 'Phil. Trans.,' vol. 210, p. 58.

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Various formulæ have been suggested for series lines. Those of Rydberg and Kayser and Runge have been shown to be not sufficiently accurate for representing observed values, and several modifications of these have been brought forward. The most promising of these is perhaps that of Hicks,* which is a modified Rydberg formula. This formula gives n, the oscillation frequency, *i.e.* the number of waves per centimetre, in the following form—

$$n = A - N/\left(m + \mu + \frac{\alpha}{m}\right)^2,$$

where N is the universal Rydberg constant, 109675, and m takes the values 1, 2, 3, etc., for the different lines of the series, the other quantities being constants for the particular substance. With the values of these constants found by Hicks for lithium, we find very good agreement for the calculated and observed values of the wave-lengths; in the last column of Table I there are given the differences between the observed and calculated wave-lengths under the heading O—C. The agreement is seen to be within the estimate of the possible error, but there is an indication that the observed values are all smaller than the calculated values. This would be accounted for by a value of the constant A, which is too small. The possible error in this constant, 43482·20, is 11·18 according to Hicks. The maximum amount allowable would make in the wave-lengths a difference of 0·06 or 0·1 to the nearest tenth of an Ångström unit. This would still leave over a small negative error in the values O—C, which may fairly be accounted for by the nature of the lines measured; they are faint absorption lines, and so not so sharp as good emission lines.

This series for lithium is interesting, as on the lines of work of Hicks, already referred to, the series is of a different type from the principal series of the other alkali metals. This difference is discussed by Hicks in the paper already cited. From the physical point of view, however, the series seems to behave just like the series in the cases of the other alkali metals. The set of lines appears under very similar conditions as absorption lines, taking account of the higher temperature required for volatilisation of the lithium, and the series is accompanied by the channelled space spectrum as is the case with sodium and potassium. The earlier members of the series are easily reversed in the arc, and anomalous dispersion effects appear in transmitted light for wave-lengths in the neighbourhood of the series lines. In these respects the physical characteristics of these lines are exactly like those exhibited by the corresponding lines in the cases of the other metals.

* *Loc. cit.*

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It is difficult then to see what the meaning of the difference in type as discovered by Hicks can be.

It may be remarked in this connection that the values for the constants A of the Hicks formula, that is the wave numbers of the heads of the series, viz., Li 43482, Na 41446, K 35006, Rb 33687, Cs 31400, continually decrease as the atomic weights increase, so that we cannot attach too much importance to the fact that the first members of these series do not fall into such regular order, the number for lithium being apparently out of place. It may also be mentioned that the order into which the wave numbers of the first members of the series fall for the elements other than lithium does not show any close relation to the atomic weights.

In a note from Prof. Hicks he has pointed out that in the wave-lengths for the cæsium principal series lines published in a paper I communicated to the Royal Society in January, 1910, there are probably some errors in the determinations, as some of the later lines of the series show departures from the values which seem probable as calculated from his formula. I have made a re-determination of these lines from photographs of the absorption spectra for cæsium vapour set free by the action of sodium and potassium on the chloride of cæsium. I have not been able to obtain metallic cæsium, and the presence of the vapour of the other metals rather obscures the absorption lines due to the metal. With some better photographs a few more lines have been measured, extending the list to 24 for the principal series. With the vapour of cæsium itself there is not much doubt that a considerably larger number of the lines could be observed.

The following table gives the re-determinations of wave-lengths for the lines from No. 8 of the series; 22, 23, and 24 are new lines. With regard to the accuracy of determination of those measurements, it is not so good as for the lithium lines, as there is considerably more dispersion in the region occupied by these latter, so that we can estimate the possible error as 0·5 of an Ångström unit. In the third column is given the difference between the observed and calculated values of the wave-length, the calculated value being obtained from the Hicks formula,

$$n = 31400{\cdot}16 - \mathrm{N}/\left(m + 1{\cdot}450967 - \frac{0{\cdot}090077}{m}\right)^2.$$

The comparison spectrum for this purpose was that of the iron arc.

It will be noticed that all the differences in the third column are of the same sign; a change in the constant A of the Hicks formula, sufficient to make a change of 0·5 in the limiting wave-length, would bring all these observed wave-lengths into agreement with the formula. The possible error, however,

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Table II.

m.	λ.	O−C.
8	3313·5	−0·3
9	3288·9	−0·3
10	3270·4	−0·7
11	3256·6	−0·7
12	3245·9	−0·6
13	3237·8	−0·2
14	3230·6	−0·6
15	3224·6	−0·9
16	3220·3	−0·5
17	3216·4	−0·5
18	3212·9	−0·6
19	3210·1	−0·5
20	3207·7	−0·1
21	3205·6	−0·4
22	3204·0	−0·2
23	3202·4	−0·1
24	3200·7	−0·4

in A of the formula cannot be determined, for the observations used in its calculation have not their possible errors ascribed to them.

Dispersion in Vapours of the Alkali Metals.

By Prof. P. V. Bevan, M.A., Royal Holloway College.

(Communicated by Sir J. J. Thomson, F.R.S. Received January 20,—Read March 9, 1911.)

[Plates 6 and 7.]

In the 'Proceedings' of the Royal Society, A, vol. 84, p. 209, I gave an account of experiments with Potassium vapour, which had for their object the determination of the dispersion curve for the vapour. The effect of the first three pairs of lines of the principal series was quantitatively estimated, and it appeared that certain conclusions could be drawn as to the numbers of systems taking part in the absorption of light. The present communication deals with further experiments of the same kind with vapours of Sodium and Rubidium, and again with the vapour of potassium, as far as regards a temperature effect, which will be discussed later. The experiments were made possible by a grant from the Royal Society, which enabled me to obtain metallic rubidium, and I am glad to take this opportunity of thanking the Government Grant Committee.

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In a former paper* I gave results of the measurements of wave-length of the principal series lines for rubidium obtained in the absorption spectrum. This spectrum was obtained by heating rubidium chloride with metallic potassium; enough vapour was formed to give an absorption spectrum showing 25 lines of the series. With metallic rubidium it is easier to get the absorption spectrum, and the list of lines has been extended to include 30 members. A better reading microscope has been available since the original measurements, so that the complete series of lines has been remeasured. The method adopted was the same as that described in the paper referred to, so that there is no need for further description.

The following table gives the measurements of the wave-lengths of the lines of the principal series. The first four members have been measured by Kayser, and the fifth by Ramage. The sixth member appears in some photographs as a pair, but the two lines are close together, and generally broadened somewhat, so that the readings cannot be made so accurately as for later members of the series.

Wave-lengths of Lines of the Principal Series for Rubidium.

1	7950·46	7	3112·95	19	2991·12
	7805·98	8	3082·39	20	2988·94
2	4215·72	9	3060·62	21	2987·01
	4201·98	10	3044·33	22	2985·45
3	3591·74	11	3032·20	23	2984·05
	3587·23	12	3022·72	24	2982·68
4	3351·03	13	3015·16	25	2981·51
	3348·86	14	3009·03	26	2980·52
5	3229·26	15	3004·11	27	2979·62
	3228·18	16	2999·96	28	2978·81
6	3158·25	17	2996·51	29	2978·10
	3157·69	18	2993·52	30	2977·39

With the measuring instrument used, the lines 10–30 should not have any error as great as 0·1 Ångström unit. The measurements were made to 0·01 unit, and are expressed here to that order, but the last figure is not reliable. The lines 8 and 9 could not be determined accurately, but should be within 0·2 of the correct value. In 6 and 7 the accuracy is still less, but there should not be a greater error than 0·3 tenth-metre.

[*Note.*—It is interesting to compare the values of the wave-lengths for the principal series lines of rubidium with the values as given by the formula proposed by Hicks.† For rubidium this formula is

$$n = A - \frac{N}{(m+\mu+\alpha/m)^2},$$

* 'Roy. Soc. Proc.,' A, vol. 83, p. 421.

† W. M. Hicks, 'Phil. Trans.,' A (190), vol. 210, p. 57.

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where N is the universal Rydberg constant 109675, A is 33687·5, μ is 1·366399 for the more refrangible of the pairs of lines and 1·353346 for the less refrangible member, and α is −0·074554 and −0·074382 for the pairs of lines. For lines as high as the sixth of the series account of the difference in the values of α need not be taken. In the observed values the difference between the two members of each pair is not to be detected after the sixth member, and it is therefore a little difficult to decide what exactly to take as the calculated values. The more refrangible component of a pair is the more intense where the members are separable, and therefore the observed value of the centre of the line, where the two appear as one, is probably rather nearer the more refrangible component. In the following list the differences (Observed—Calculated) are given for the one observed and two calculated values after the sixth of the series.

No. of line pair.	O−C.	No. of line pair.	O−C.	No. of line pair.	O−C.
6	−0·19 −0·03	15	−0·11 −0·05	23	+0·05 +0·07
7	−0·31 +0·18	16	−0·11 −0·06	24	−0·06 −0·04
8	−0·17 +0·16	17	−0·08 −0·04	25	−0·09 −0·08
9	−0·11 +0·13	18	−0·14 −0·10	26	−0·08 −0·07
10	−0·29 −0·11	19	−0·01 +0·02	27	−0·07 −0·06
11	−0·18 −0·04	20	−0·02 0·0	28	−0·07 −0·06
12	−0·15 −0·04	21	−0·07 −0·05	29	−0·05 −0·04
13	−0·15 −0·06	22	+0·01 +0·03	30	−0·10 −0·09
14	−0·18 −0·11				

The formula gives very good agreement with the observed values for the pair 6; for 7, 8, and 9 the observed value is between the two calculated values; 10 is not in such good agreement, the observed value being outside the two calculated values, but by very little. The other lines are in good agreement, on the whole, the observed values lying a little to the side of lower wave-length, but in all cases the departure is not more than the estimated possible error. A slight alteration of the constant A such as is possible according to Prof. Hicks' calculations could adjust this. The difference between the wave-lengths of the pairs of lines is considerable up to about the 13th pair in the series, and it ought to be possible to measure the separate members. I hope to be able to do this in the future; measurements of such a character would have considerable interest.]

Fig. 1, Plate 6, is a photograph of a series of the absorption spectra

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of Rubidium vapour. The vapour was of increasing density for the spectra 1 to 6, after this at decreasing density. The principal series lines are the most evident feature. The continuous absorption for wave-lengths less than the limit of the series is noticeable in 1, 2, 3, especially. This phenomenon is similar to that observed by Wood in the case of sodium. The broadening of the lines is also very evident in the spectra of the denser vapour. Some of the potassium lines appear in these photographs owing to the presence of this metal as impurity.

Rubidium also possesses a channelled-space spectrum, very similar to the spectra of sodium and potassium. This consists of a very large number of lines, with strong absorption at certain intervals, giving the appearance of bands with sharp edges. This spectrum was photographed with a small diffraction grating and laboratory spectrometer, the telescope being replaced by a camera. The aperture and grating being small, detailed examination of the spectrum was impossible, but the wave-lengths corresponding to the heads of the bands were determined. For comparison, the neon red spectrum was used. Three lines were found in this which were not to be discovered in the list of neon lines by Baly. The wave-lengths of these lines are 7032·86, 6929·50, and 6334·61. I have not been able to identify these lines with any belonging to other elements, and assume that they are new lines. The wave-lengths of the edges of the rubidium bands are as follows:—

6734·0	6774·9	6821·0	6871·9
6754·0	6796·0	6844·2	6898·1

The ratios of these numbers to 7950, the wave-length of the line of the first pair of the principal series with greatest wave-length, range from 0·8470 to 0·8676. The corresponding ratios for sodium range from 0·8112 to 0·8706, and for potassium, from 0·8328 to 0·8602.* Carter† has measured the lines of the potassium spectrum, and has given a table with lines marked "very strong" and "strong." These are similar to the lines obtained from Wood's work on sodium, and so may be taken as the edges of the bands. These give numbers for the ratios ranging from 0·8193 to 0·8502. It is an interesting fact that these numbers all fall within the same range. With more light available, more of this type of line would appear for rubidium, and the correspondence be closer still. It is curious that the ratios agree for the more refrangible of the first pair of the principal series—if the less refrangible line be taken, we have no obvious correspondence. Lithium also

* 'Phil. Mag.,' January, 1910, p. 199.
† 'Physical Review,' vol. 27, 1908.

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shows a similar spectrum, situated in the same region, relative to the red lithium line.

There are other points of interest in the rubidium absorption spectrum notably, in the way in which the lines broaden with denser vapour, and in the appearance of lines which seem associated with the principal series lines. These points are, however, still under investigation.

For the dispersion of light due to rubidium vapour, the same method was adopted as was described in the paper already referred to. The vapour prism was in a tube with quartz plates for its ends, and the crossed prism system adopted. The achromatic lens described in the former paper was again used. This lens proves very satisfactory with a small aperture—a larger aperture allows a considerable amount of spherical aberration to spoil the definition. With this lens, an image of a horizontal slit, illuminated by an arc light, is thrown on the slit of the spectrograph. This, without the metallic vapour, gives a linear spectrum. On placing the tube, with metallic vapour in it, in the beam of light, vertical dispersion takes place, and the dispersion curve is seen in the spectrograph. With the quartz spectrograph used there is very little dispersion at the red end of the visible spectrum, but sufficient for photographs to be taken, which showed the complete dispersion curve over a range including all the lines of the principal series except the first pair. The main features of the phenomena to be observed are very similar to those described in the case of the similar experiments with potassium vapour. In the case of rubidium, the pairs of lines are more widely separated than with potassium, so that it is easier to observe the region between the lines of a particular pair. The dispersion effects can be detected on photographs at the first eight members of the series. Measurements could be made at the first four members, which were fairly reliable. At the next two members measurements could be made, but these could only be regarded as giving the order of the effect. As before, the quantities measured were the displacements of the spectrum from its undeviated position at various wave-lengths. These quantities when reduced—to allow for the "tilt" of the plate in the spectrograph—are proportional to the deviation of the rays by the vapour prism, and so are proportional to $n-1$ when n is the refractive index; n being very nearly 1, this is again proportional to n^2-1, and so to the well-known expression of the Sellmeier dispersion formula.

For rubidium, the early lines of the series being pairs separated by a considerable amount, it was found impossible to treat the pair of lines as a single line at a mean position. The case is thus more complicated than

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that of potassium, as two constants are required for each pair of the series. It appeared that the ratio of these constants for a pair of lines was approximately constant throughout the series. This conclusion is only tentative, as the determination of the ratio of these constants is a matter of considerable difficulty. A very small error in a wave-length used for the determination makes a considerable change in the value of the constant. However, it was assumed that the ratio was the same and this was determined from observations at the second pair of lines. No reliable measurements could be made at the first pair, as the dispersion available was so small. This constant then being determined, its value was assumed for the other pairs, and the values of the separate constants deduced from the observations.

The dispersion formula of Sellmeier for this case can be written

$$n^2-1 = \Sigma\left(\frac{m_1\lambda^2}{\lambda^2-\lambda_1^2}+\frac{m_1'\lambda^2}{\lambda^2-\lambda_1'^2}\right),$$

when λ_1, λ_1', are the wave-lengths of the pair of lines, and m_1, m_1', the corresponding constants.

The effect due to the first pair of absorption lines is far larger than that due to succeeding pairs, so that, as was done in the case of potassium, the main part of the dispersion curve—that not in the immediate neighbourhood of the second, third, etc., pairs of lines—was determined first and then detailed observations were made in the regions of the pairs of lines. Several different photographs were used, as those suitable for one region might not be suitable for other parts. The deviations were reduced so as to all be measured on the same scale. With vapour of sufficient density to show the effect at the second and later pairs of lines the red end of the visible spectrum is almost completely absorbed down to a wave-length of about 6400.

The following tables give the measurements of deviations (corrected and reduced to the same scale) for the corresponding wave-lengths.

I.—Deviation for Main Portion.

Wave-length.	Deviation.	Wave-length.	Deviation.
3047	0·6	4500	1·5
3135	0·7	4730	1·9
3190	0·8	5070	2·6
3250	0·9	5500	3·5
3445	0·9	5890	4·9
3969	1·4	6100	5·9
4020	1·5	6350	7·4
4181	2·6		

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II.—Deviations near Lines 4202, 4216.

a.		*b*.			
Wave-length.	Deviation.	Wave-length.	Deviation.	Wave-length.	Deviation.
4132·5	−1·65	3933·8	−1·5	4214·5	−2·7
43·7	−1·75	68·6	−1·5	15·0	−3·0
54·5	−1·84	4158·0	−2·0	15·5	−4·0
72·2	−2·05	68·0	−2·2	17·5	+2·7
77·7	−2·2	81·0	−2·5	19·0	2·0
81·8	−2·47	86·0	−2·7	20·0	1·7
87·5	−2·75	90·0	−3·0	20·5	1·3
91·6	−3·2	92·5	−3·3	21·5	1·0
95·5	−4·3	96·5	−4·0	22·0	0·7
98·4	−6·2	98·5	−5·0	23·0	0·3
99·2	−7·3	4200·5	−6·7	24·0	0·0
4210·5	+0·6	1·5	−8·3	30·0	−0·7
19·5	−0·6	6·0	+2·3	37·0	−1·0
22·6	0·0	7·5	1·7	50·0	−1·2
27·6	+0·5	8·5	1·0	75·0	−1·3
50·6	1·15	9·0	0·7	4308·0	−1·5
60·6	1·15	10·0	0·3	25·0	−1·5
71·6	1·2	11·0	0·0	84·0	−1·7
82·6	1·15	11·5	−0·3	4405·0	−1·7
94·3	1·3	12·0	−0·7		
99·4	1·3	12·5	−1·0		
4308·0	1·4	12·8	−1·3		
25·9	1·6	13·0	−1·7		
83·7	1·6	13·5	−2·0		
4404·9	1·6	14·0	−2·3		

In Table II, *a*, the wave-lengths are of iron lines. The first horizontal slit was illuminated by an iron arc and so the deviated spectrum consisted of points corresponding to the iron lines. In this way the wave-lengths were accurately known, but the spots on the negative were somewhat blurred and the deviation measurements were not so reliable as in *b*, which consists of measurements made on a photograph taken with the ordinary carbon arc. The deviations have been reduced so that all are on the same scale as that of Table I.

III.—Deviations near Lines 3587, 3592.

Wave-length.	Deviation.	Wave-length.	Deviation.
3538	−1·0	3590·47	−1·0
3556	−1·2	3591·28	−1·3
3580·9	−1·4	3591·74	
3583·4	−1·8	3592·36	+0·6
3584·8	−2·2	3592·55	+0·2
3585·6	−2·5	3592·90	−0·2
3586·1	−2·9	3593·44	−0·4
3586·4	−4·2	3594·65	−0·6
3587·2		3595·86	−0·8
3589·0	+0·6	3600·7	−1·0
3589·3	−0·2	3622·9	−1·0
3590·06	−0·6		

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IV.—Deviations near Lines 3349, 3351.

Wave-length.	Deviation.	Wave-length.	Deviation.
3339·5	−0·9	3351·3	−0·1
3344·8	−1·0	3351·7	−0·3
3347·1	−1·1	3352·3	−0·5
3347·6	−1·3	3355·8	−0·7
3348·2	−1·7	3365·0	−0·8
3350·0	−0·5		

V.—Deviations near Lines 3228, 3229.

Wave-length.	Deviation.	Wave-length.	Deviation.
3225·1	−0·8	3228·7	
3226·8	−1·0	3229·4	−0·6
3227·2	−1·4	3232·6	−0·7
3227·4	−1·6	3238·1	−0·8

VI.—Deviations near Line 3158.

Wave-length.	Deviation.	Wave-length.	Deviation.
3155·4	−0·8	3158·6	−0·4
3157·1	−1·0	3159·6	−0·6
3157·6	−1·3	3163·1	−0·8

By plotting the main curve and deducting the values of deviation corresponding to the first pair of lines from the observations near succeeding pairs, we obtain the deviation at various wave-lengths as far as they depend on any particular pair of the series, for the influence of any pair after the first is confined to the immediate neighbourhood of the lines. In this way we obtain the observed deviations, which are proportional to the quantity

$$\frac{m_2\lambda^2}{\lambda^2-\lambda_2^2}+\frac{m_2'\lambda^2}{\lambda^2-\lambda_2'^2},$$

and the corresponding quantities for higher members of the series.

From these quantities we can find the values of the constants m_2, m_2', etc. With the large number of observations made it was a little difficult to decide how to obtain the best values of the constants. The method of least squares would have been laborious, and, as the observations are of very varying weights, it was thought that no great advantage would be obtained by applying it. Near the absorption lines slight errors in wave-length determination would involve large errors in the calculated constants, and

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where these errors would be small, at some distance from the absorption lines, the small deviations become uncertain in measurement. It is difficult to balance these two sources of error, so the method adopted was to plot all the observations and find values of the constants which gave a curve fitting the observations as well as possible. The two constants m and m', as has already been remarked, seemed to have about the same ratio for each pair of lines, so that this ratio was determined once for all from the observations in Table II for the second pair of lines and was assumed to be the same for the other pairs.

The values of the constants obtained are as follows :—

Constants.	Corresponding wave-lengths.	Constants.	Corresponding wave-lengths.
1 $\begin{cases} m_1 = 2{\cdot}71 \\ m_1' = 0{\cdot}90 \end{cases}$	7805·98 7950·46	4 $\begin{cases} m_4 = 3{\cdot}0 \times 10^{-4} \\ m_4' = 1{\cdot}0 \times 10^{-4} \end{cases}$	3348·86 3351·03
2 $\begin{cases} m_2 = 7{\cdot}5 \times 10^{-3} \\ m_2' = 2{\cdot}5 \times 10^{-3} \end{cases}$	4201·98 4215·72	5 $\begin{cases} m_5 = 2{\cdot}5 \times 10^{-4} \\ m_5' = 0{\cdot}8 \times 10^{-4} \end{cases}$	3228·18 3229·26
3 $\begin{cases} m_3 = 10{\cdot}0 \times 10^{-4} \\ m_3' = 3{\cdot}3 \times 10^{-4} \end{cases}$	3587·23 3591·74	6 $\begin{cases} m_6 = 1{\cdot}5 \times 10^{-4} \\ m_6' = 0{\cdot}5 \times 10^{-4} \end{cases}$	3158·2 3157·7

The values for 5 and 6 are very doubtful, as the deviations are so small except very close to the absorption lines. For example, the observations for m_6' gave three values, 0·7, 0·5, and 0·2, multiplied by 10^{-4}. These values, therefore, can only be regarded as giving an estimate of the order of the effect.

In text-fig. 1 the dispersion curve is plotted for the range from 6300 to 3200. The region of longer wave-length is not shown, as the curve would not show the effects at the second, third, and fourth lines if on a small enough scale to show the curve at the red lines. Also, with the apparatus at my disposal, sufficient accuracy could not be obtained in the determination of wave-lengths in the red region owing to the small dispersion available. The curve represents the quantity

$$\sum_1^4 \left(\frac{m_1\lambda^2}{\lambda^2-\lambda_1^2} + \frac{m_1'\lambda^2}{\lambda^2-\lambda_1'^2} \right),$$

with the values of the constants above. The observed values of deviations are indicated by points which lie very fairly closely about the curve.

In fig. 2 (p. 68) the ordinates represent the quantity

$$\frac{m_1\lambda^2}{\lambda^2-\lambda_1^2} + \frac{m_1'\lambda^2}{\lambda^2-\lambda_1'^2} + \frac{m_2\lambda^2}{\lambda^2-\lambda_2^2} + \frac{m_2'\lambda^2}{\lambda^2-\lambda_2'^2},$$

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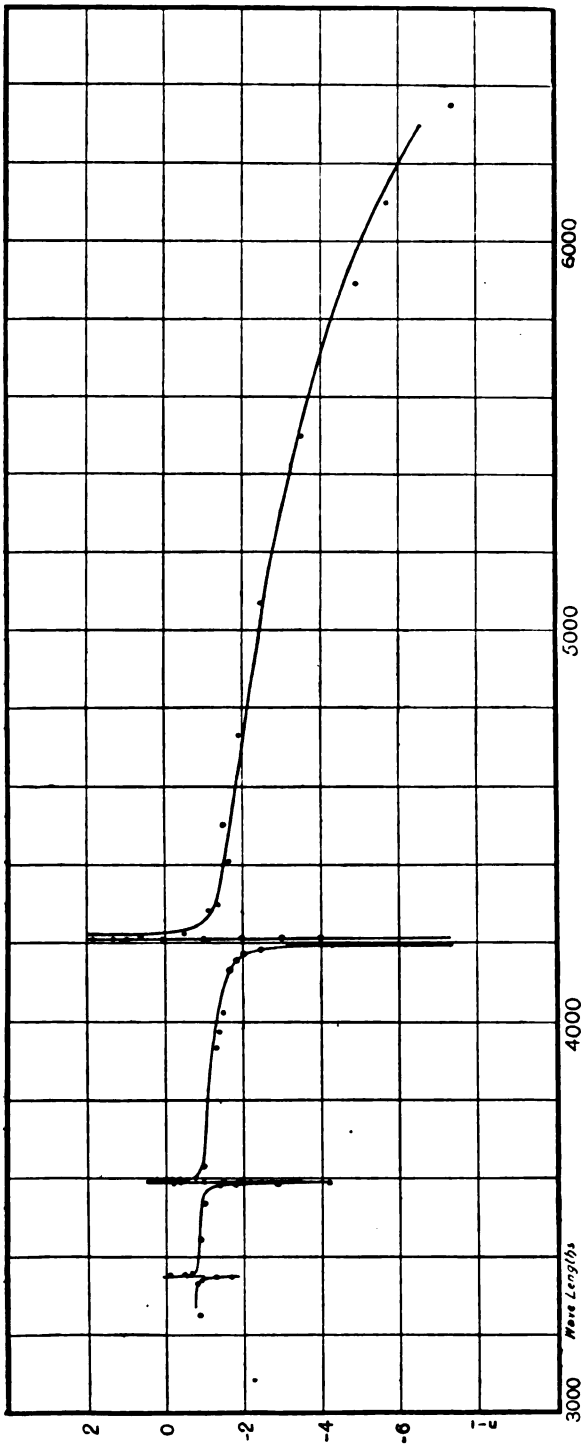

Fig. 1.—Dispersion Curve for Rubidium vapour:—

$$n-1=\frac{0\cdot90\lambda^2}{\lambda^2-7950^2}+\frac{2\cdot71\lambda^2}{\lambda^2-7806^2}+\frac{2\cdot5\times10^{-3}\lambda^2}{\lambda^2-4215^2}+\frac{7\cdot5\times10^{-3}\lambda^2}{\lambda^2-4202^2}+\frac{3\cdot3\times10^{-4}\lambda^2}{\lambda^2-3592^2}+\frac{10\cdot0\times10^{-4}\lambda^2}{\lambda^2-3587^2}+\frac{10^{-4}\lambda^2}{\lambda^2-3351^2}+\frac{3\cdot0\times10^{-4}\lambda^2}{\lambda^2-3349^2}.$$

The points marked are observed values.

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the second two terms of which we can regard as the deviation due to the second pair of the lines of the principal series. The scale is much larger than that of fig. 1. The observed deviations are represented by points and crosses. The points refer to the observations *a* of Table II, the crosses to those of *b* in the same table. The observations *a* were from a photograph with the iron arc as source of light, so that the wave-lengths are accurately known; the deviations are, however, not so good as for the observations *b*.

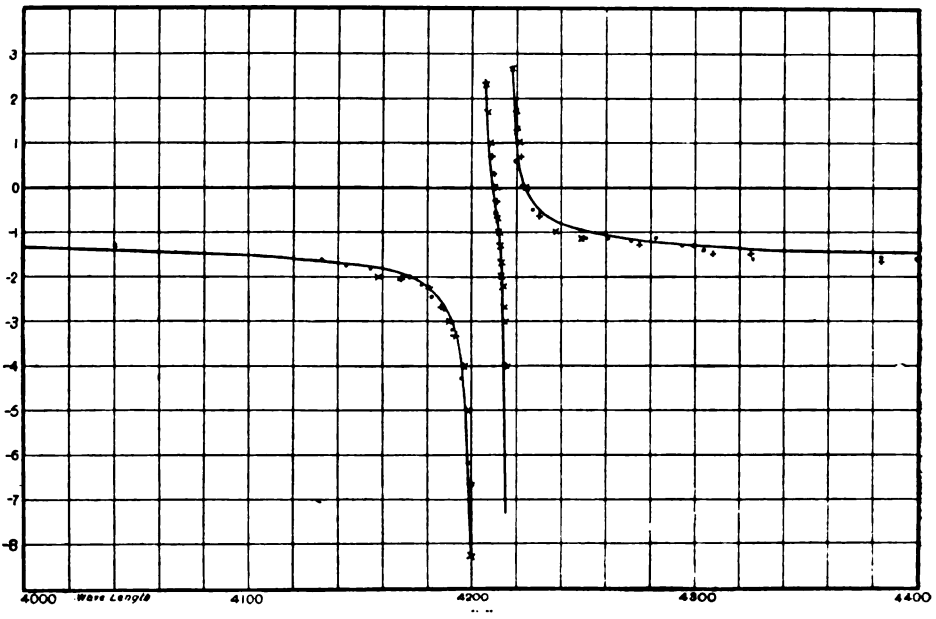

FIG. 2.—Dispersion Curve in the neighbourhood of lines 4216, 4202. Rubidium vapour.

Figs. 3 and 4 (p. 69) represent the quantities

$$\frac{m_3\lambda^2}{\lambda^2-\lambda_3^2}+\frac{m_3'\lambda^2}{\lambda^2-\lambda_3'^2} \quad \text{and} \quad \frac{m_4\lambda^2}{\lambda^2-\lambda_4^2}+\frac{m_4'\lambda^2}{\lambda^2-\lambda_4'^2},$$

so that the ordinates may be taken to represent the deviations due to the third and fourth pairs of the principal series of lines. The points represent the observations recorded in Tables III and IV.

In this series of curves the points representing observed deviations are found to lie very fairly closely about the curves. Better agreement could perhaps be found if a more elaborate method of determining the constants were employed, but there seemed no reason at present for the enormously increased arithmetic necessary for an application of the method of least squares to the observations.

Fig. 2 of Plate 6 is a photograph of the dispersion effect in the neighbour-

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hood of the red lines; *b* is the photograph as taken, and *a* is an enlargement without retouching. The curve as seen in the spectroscope is very beautiful, showing the region between the two lines very clearly. This photograph was taken with a simple spectroscope with one flint glass prism, so that

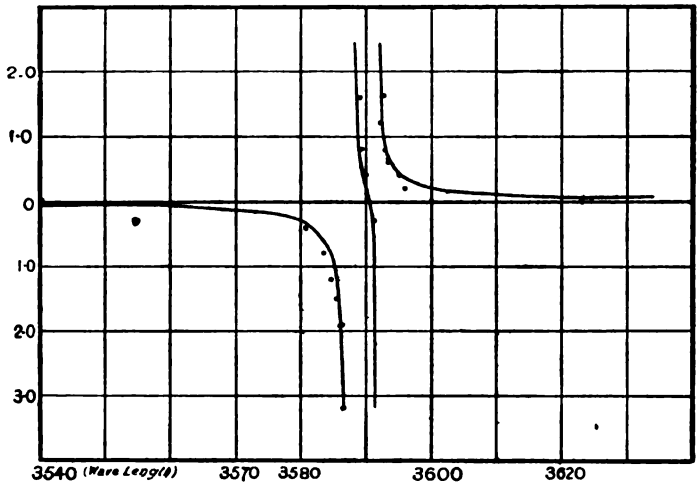

FIG. 3.—Dispersion near 3592, 3587, in Rubidium vapour.

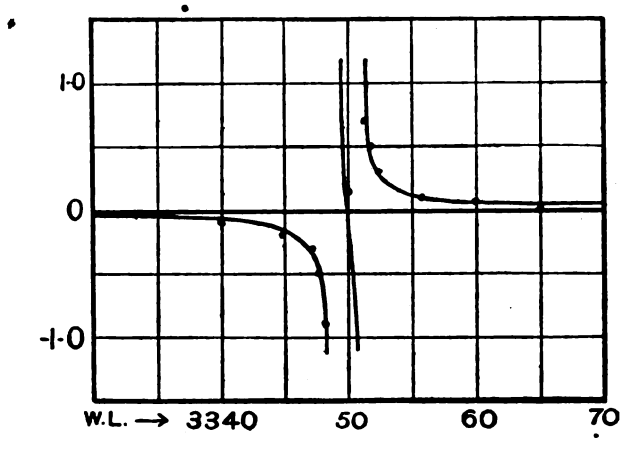

FIG. 4.—Dispersion near 3351 ; 3349.

there is very little dispersion between the lines 7950 and 7806. Fig. 3 is interesting as showing a dispersion curve for three absorption lines; the vapour for this photograph was a mixture of potassium and rubidium. Rubidium chloride was heated in a tube with potassium, and a considerable quantity of rubidium vapour set free. The dispersion was small, so that the

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two potassium lines 7699 and 7665 have effect as only one line. In fig. 2, just to the left of 7806, the slight effect of potassium as impurity in the rubidium is visible.

In Plate 7, fig. 4, two photographs of the effect at the rubidium lines 4215, 4202, are shown; *a* and *b* are enlargements of *c*; *a* is with denser vapour than *b*. To the left of the photographs the effect at the next pair of lines also appears—3591, 3587. In these photographs the potassium impurity also shows itself by the slight break at the lines 4047, 4044. Fig. 5 shows the effect at the third and succeeding pairs of lines; *a* is again an enlargement of *b*. The position of the undeviated spectrum was also photographed on this plate. This photograph shows also a good number of the absorption lines nearer the limit of the series. The potassium line at 3447 also appears. Fig. 6 gives examples of the dispersion curves photographed with the undeviated spectrum at the lines 4215, 4202, and the pair at 3590.

Sodium.

For the case of sodium the dispersion corresponding to the D lines has been investigated by Wood.* He, however, has not made measurements of the dispersion corresponding to the other lines of the principal series, and it seemed worth while to obtain values of the constants for sodium to see if there might be a general relation to be found in the values of these constants for the alkali metals. Wood has investigated the dispersion between and near to the D lines, but his numbers do not enable us to obtain any reliable value of the ratio of the two separate constants for the D lines. All that can be said is that the constant for the line of smaller wave-length is greater than the other, in accordance with the observed results for rubidium and potassium, and with the fact that the line of shorter wave-length of all the pairs of these series for the alkali metals is more intense than the other.

Sodium is, for dispersion near lines other than the D lines, more difficult for investigation than the other metals of the group except lithium. This is owing to the fact that a higher temperature is necessary to obtain the vapour in sufficient density. With sodium, however, the first pair of the principal series is in a more suitable part of the spectrum for visual observation and also for photographic methods, the red end, where the potassium, rubidium, and cæsium lines occur, being more difficult to see and photograph than the yellow. The dispersion effects could only be measured with any accuracy at the lines 3304 and 2853. The effect could be observed

* 'Phil. Mag.,' [6], 1904, vol. 8, p. 293.

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at the two next pairs of lines, but no reliable measurements could be made. For the sodium measurements, instead of a slit as source of light, the naked arc was used, with a grating of fine wires wound on a wooden frame in front of this. The plane of the wires being nearly horizontal, they were at different distances from the lens used to focus them on the slit of the spectroscope, so that with a rough adjustment of focus some of the images of the wires would be in good focus on the spectroscope slit after the heated tube was introduced. This device saved a good deal of trouble in focussing.

The following table gives the results for deviations and wave-lengths:—

Wave-length.	Deviation.	Wave-length.	Deviation.	Wave-length.	Deviation.
5760	134	3372	0·6	2900	0
5620	59	3322	1·9	2865	0·2
5550	47	3317·4	2·4	2857·7	0·7
5410	31	3313·4	4·4	2856·7	1·1
5300	20	3312·2	5·4	2855·3	2·5
4500	9·2	3309·3	6·4	2854·3	3·7
4450	6·5	3295·9	−5·1	2851·8	−3·0
4220	6·4	3294·3	−4·1	2850·9	−1·7
3970	4·9	3292·3	−3·1	2849·5	−0·8
		3288·7	−2·6	2845·5	−0·3
		3274	−1·6	2800	0
		3200	−0·3		

The deviations in the second two columns are from the mean position of the curve, not the whole deviations; they represent, therefore, the quantities

$$\frac{m_2\lambda^2}{\lambda^2-\lambda_2^2}, \quad \frac{m_3\lambda^2}{\lambda^2-\lambda_3^2},$$

λ_2, λ_3, being the mean wave-lengths of the second and third pair of lines for the sodium series.

The deviations in the first column give the data for the main part of the dispersion curve,

$$n^2-1 = \frac{m_1\lambda^2}{\lambda^2-\lambda_1^2}, \ \lambda_1 \text{ being } 5890.$$

Using the measured deviations instead of n^2-1 we obtain for m_1 for this set of observations 5·85. From the other deviations we obtain $m_2 = 2{\cdot}30 \times 10^{-2}$ and $2{\cdot}92 \times 10^{-3}$. In fig. 5, I, the curve is traced with these values of the constants, and the observed values of deviations marked by crosses. These points, near the lines 3303, 2853, were obtained by adding the observed deviations of the above table to the calculated value, taking only the first term of the Sellmeier formula. In other words, the observed deviations are only observed partly—their values measured from the position

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corresponding to the deviation produced by the first line. In Curve II, fig. 5, the part of the curve nearer the D lines is drawn. The scale for this curve is much smaller than for I, and is shown on the right-hand side of the diagram. It will be noticed that the point representing deviation at 5300 does not lie on the curve, and its departure is greater than was to be expected. The deviation at 4500 is also off the curve in the opposite sense, though here it is possible the departure from the curve might be explained as a bad measurement. These two positions are just at the ends

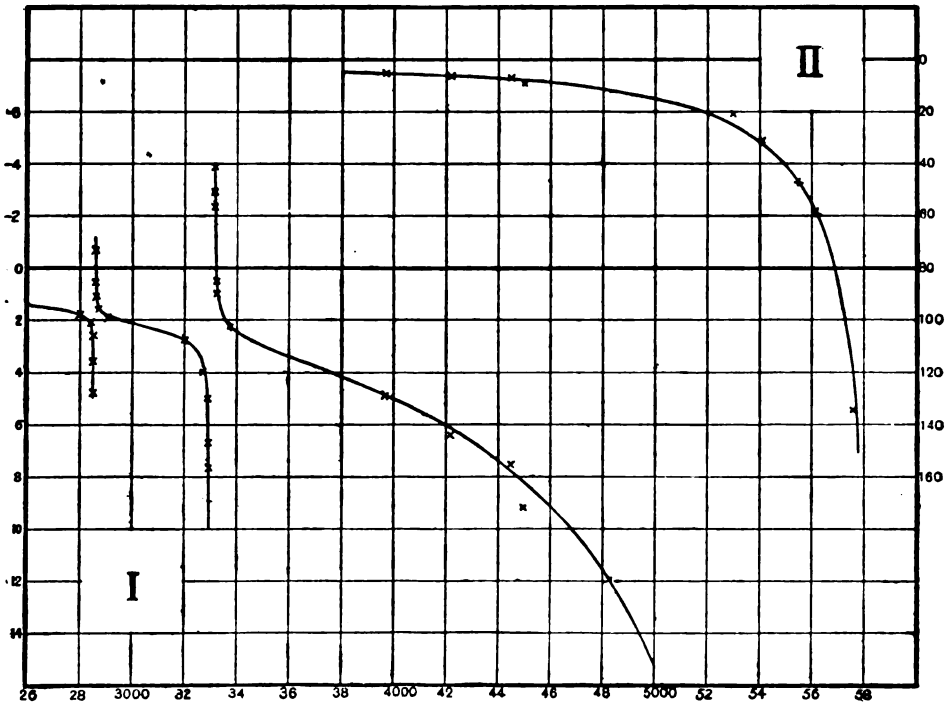

Fig. 5.—Dispersion curves for sodium vapour.

of the channelled space absorption spectrum, investigated by Wood, and for the present case this region was almost completely dark, practically all the light being absorbed. We should expect a band of this sort to involve changes in the dispersion, and these observations seem to indicate this—the departures of the points from the normal deviation are in the right direction. I have observed a similar phenomenon in the case of potassium near the corresponding absorption region, but the point wants further investigation.

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The Question of the Effect of Temperature on the Relative Values of the Constants of the Dispersion Formula.

If attention be confined to the effects of dispersion near any single pair of lines, the constant of the dispersion formula appropriate to this line increases with the temperature of the vapour used. It is not quite clear whether it is the density gradient or the prismatic form of the vapour in the tube which produces the dispersion effect, or whether both of these causes co-operate. I am inclined to think that the second effect is of most importance, but in any case, if the tube is heated more strongly, we get a vapour of greater average density and so greater dispersion effects. The question naturally occurs as to whether the different constants change proportionally with this change of average temperature in the vapour. On the view that was put forward in my earlier paper,* to which reference has already been made, that different specialised atoms are engaged in the absorption of the different lines, it seems probable that the relative numbers of these special atoms should depend on the temperature of the vapour. If more complex systems are required for the absorption corresponding to higher members of the series of lines, it seems likely that the relative number of atoms corresponding to the higher members should decrease with increase of temperature. We should expect, therefore, a change in the relative values of the constants m_1, m_2, etc., which would appear as an increase in the ratios m_1/m_2, m_2/m_3, etc., with increase in temperature. An effect of this kind was therefore sought in the case of potassium and sodium. As will appear, there is evidence for an increase in these ratios which is fairly conclusive. The actual determination of the constants has, of course, a considerable amount of uncertainty, but a large number of measurements were made, and there does seem to be a definite increase in the ratios indicated. For the case of sodium three photographs were used with different densities of vapour. For the most dense vapour the absorption was complete in the region 5000 to 4600. This photograph was the one used for the measurements for the sodium dispersion curve already described. The next of the series of three gave dispersion in the region near the D lines of rather less than one-half that occurring in the first. On this photograph measurements could be made giving fairly good values of the constants corresponding to the first three lines of the series. The third photograph was with vapour of considerably less density, and the effect at the third line was too small for any reliable measurements. Measurements of deviations were made at a number of points near the absorption lines, so that several of the values of the constants could be obtained.

* 'Roy. Soc. Proc.,' A, vol. 84, p. 209.

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The following tables give the observed values of the constants; all observations are taken into account, excepting in cases where the measurement was clearly bad, owing either to the deviated spectrum being indistinct, or the wave-length at the particular position differing so little from that of the absorption line that the effect of the possible error in its determination was too large :—

Sodium (1).

m_1	6·00	5·94		
	5·96	5·67		
	5·75	5·89		Mean, 5·85
	5·92	5·77		
	5·83			
	5·81			
$m_2 \times 10^2$.....	2·44	2·15	2·18	
	2·31	2·04	2·10	
	2·49	2·17	2·16	Mean, 2·30
	2·64	2·32	2·12	
	2·76	2·20	2·46	
	2·27	2·10		
$m_3 \times 10^3$.....	2·35	2·75	3·12	
	2·47	3·24	3·46	
	2·53	3·18	3·33	Mean, 2·92
	2·89	2·50		
	2·90	3·19		

Sodium (2).

m_1	2·36	2·18	2·25	
	2·26	2·35	2·36	
	2·34	2·19	2·27	Mean, 2·24
	2·02	2·32		
	1·99	2·50		
$m_2 \times 10^2$ ...	1·09	1·09	0·98	
	1·01	1·00	1·11	
	1·00	0·98	0·96	
	1·02	1·01	0·92	Mean, 1·02
	1·02	1·01	1·08	
	1·02	1·08	0·97	
	1·10	0·99		
	1·09	0·96		
$m_3 \times 10^3$.....	1·36	1·27		
	1·42	1·35		Mean, 1·33
	1·23	1·36		

Sodium (3).

m_1	0·493	0·516	
	0·479	0·500	
	0·520	0·515	Mean, 0·499
	0·472	0·498	
$m_2 \times 10^3$.....	2·15	1·98	
	2·54	2·50	
	2·60	2·68	
	2·04	1·92	Mean, 2·36
	2·46	2·44	
	2·50	2·50	

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We obtain from the mean values of these constants the following table:—

	(1).	(2).	(3).
m_1/m_2	254	220	211
m_2/m_3	7·9	7·7	

The difference between the ratio m_1/m_2 in the two cases (1) and (2) is considerable, and although the individual values of the constants differ in any particular case by considerable amounts, yet the indication of a decrease in the ratios is fairly strong.

In the case of potassium the evidence is rather stronger. A series of three photographs was taken with potassium with decreasing density of vapour. Clearer definition was obtained in the potassium photographs; the device of the wire grating was used for these. An example of the type of photograph is represented in fig. 7, Plate 7.

The following are the results:—

Potassium (1).

m_1	38·2		
	36·0		
	35·0		Mean, 36·4
	36·5		
	36·4		
$m_2 \times 10^2$	5·93	6·35	
	5·62	6·18	
	6·00	6·60	Mean, 6·21
	6·25	6·50	
	6·25	6·48	
$m_3 \times 10^3$	5·45	5·37	
	5·35	5·52	
	5·15	5·42	Mean, 5·45
	5·50	5·75	
	5·51		

Potassium (2).

m_1	4·65	4·76	
	4·63	4·70	Mean, 4·63
	4·65	4·75	
	4·40	4·54	
$m_2 \times 10^3$	9·17	8·65	
	9·09	9·25	Mean, 9·15
	9·55		
	9·20		
$m_3 \times 10^3$	1·32		
	1·14		Mean, 1·36
	1·40		
	1·56		

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Potassium (3).

m_1	2·36	2·47	
	2·26	2·53	Mean, 2·42
	2·32	2·52	
	2·44		
$m_2 \times 10^3$	6·59	6·64	
	6·51	6·24	Mean, 6·43
	6·29	6·29	
$m_3 \times 10^4$	7·2	9·3	
	8·7	10·5	Mean, 9·2
	9·8	9·6	

These numbers give us the following table for the ratios m_1/m_2, m_2/m_3:—

	(1).	(2).	(3).
m_1/m_2	587	507	376
m_2/m_3	11·2	6·7	7·0

The values of the constants in (1) are the best; in this case the measurements of deviation were largest, and so admit of fair accuracy. For the measurements (2) the accuracy is fairly good for m_1 and m_2; m_3 is, however, uncertain, wide differences occurring in the four values obtained. For (3) m_1 and m_2 are fairly good values, but m_3 again shows wide variations in the individual numbers. Still, allowing for the uncertainty in the observations, the diminution in the numbers for m_1/m_2 and the greater value of m_2/m_3 for (1) indicates pretty clearly that there is a real change in the relative values of the constants. The values 6·7 and 7 for m_2/m_3 from (2) and (3) are so near together, and the individual differences in the values of m_3 for (2) and (3) are so great, that the apparent increase from 6·7 to 7 is of no significance.

These numbers for potassium with those of a similar character for sodium seem to indicate a real change dependent on the temperature of the vapour.

This being so, we cannot expect any relation between the constants of the different metals, as before any such relation should appear we must have the vapours of the metals at corresponding temperatures, and as yet there is no evidence to show at what temperatures we should expect correspondence to exist.

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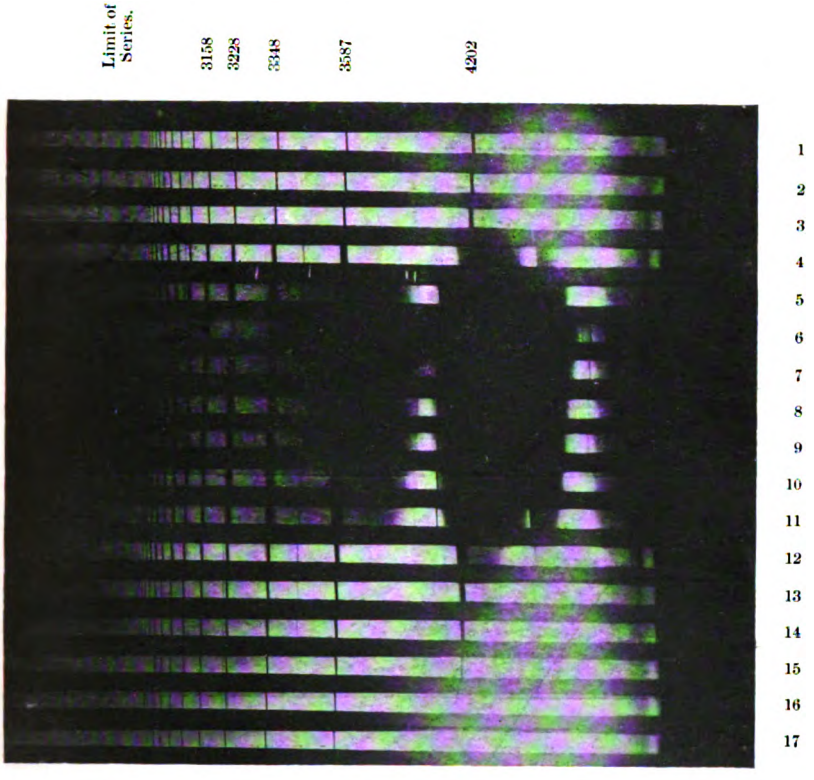

FIG. 1.

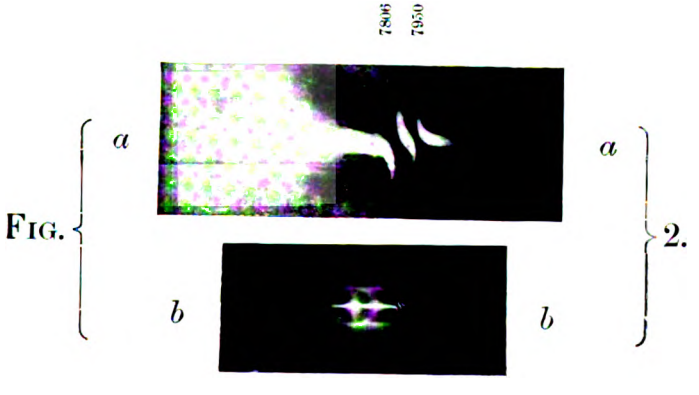

FIG. 2.

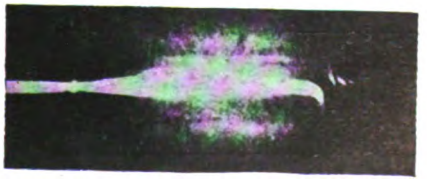

FIG. 3.

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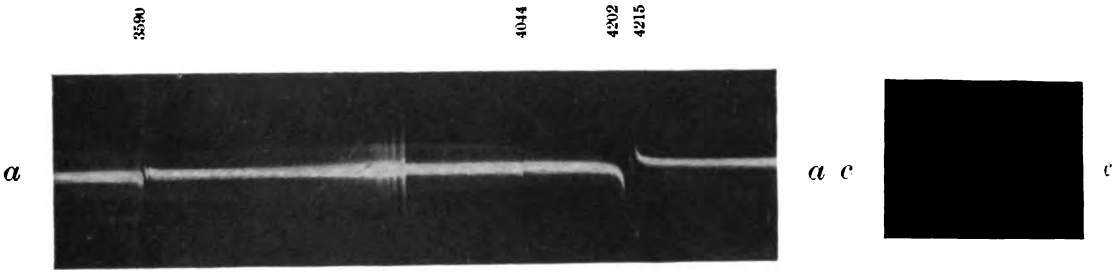
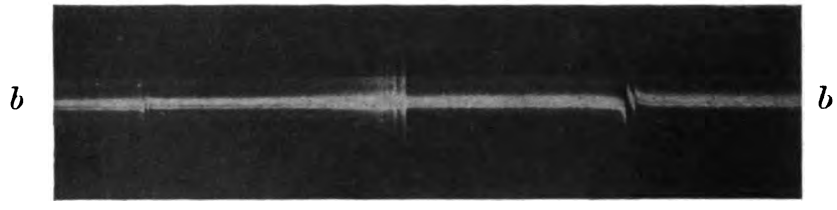


FIG. 4.



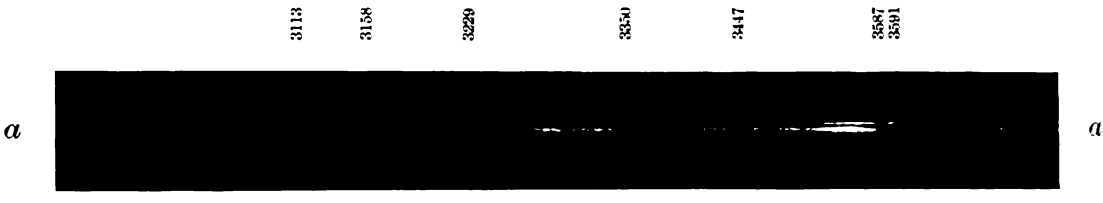


FIG. 5.

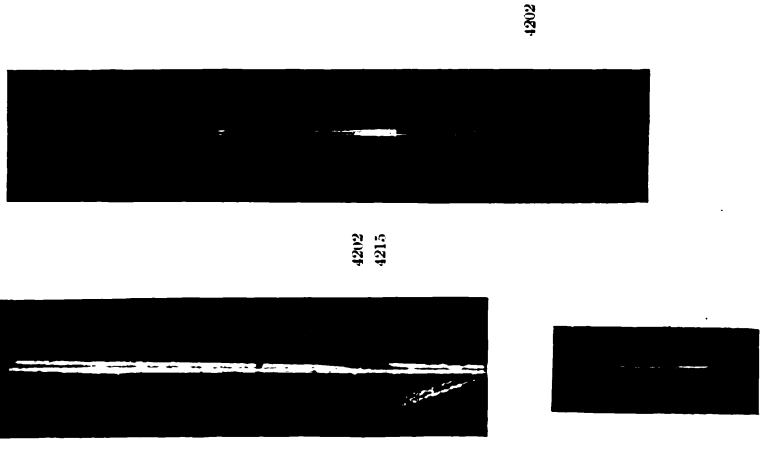


FIG. 6.

FIG. 7.

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*Report on the Separation of Ionium and Actinium from Certain Residues and on the Production of Helium by Ionium.**

By B. B. Boltwood, Ph.D., John Harling Fellow, University of Manchester.

(Communicated by Prof. E. Rutherford, F.R.S. Received February 4,—Read February 23, 1911.)

The material consisted of certain substances separated from 500 kilos. of pitchblende residues purchased by the Royal Society from the Vienna Academy of Sciences, and treated at the works of the Armet de Lisle at Nogent-sur-Marne, in France, for the removal of the radium contained in them. The operations to be described were carried out with that portion of the residual material returned to the Royal Society as "actinium residues." The material consisted of a wet paste, and was a heterogeneous mixture containing considerable proportions of lead chloride and gelatinous silica and small proportions of copper, zinc, iron, tin, and other elements.

* *Note by Prof. E. Rutherford, F.R.S.*—In 1907 the Royal Society kindly allowed me to test the actinium residues in their possession. Preliminary observations on a small fraction of the dried residue showed that it gave off the actinium emanation freely, and contained a small quantity of radium. Observations on the rate of growth of radium in the part of the residue obtained in solution showed that the amount of ionium present was less than 1/10 of the amount to be expected if all the ionium in the uranium residues had been separated with the actinium. This is borne out by the result of the chemical separation of the ionium, which is described in the paper. This result was disappointing, and indicates that the greater part of the ionium was lost in some part of the process to which the main pitchblende residues had been subjected. As there was no definite published information as to the best method of separation of actinium and ionium from such residues, it was necessary to devise suitable methods. Preliminary observations in this direction were made by Dr. Ritzel, a research student in the laboratory. These were continued by Mr. Greenwood, who carefully examined the activity in the form of thin films of definite small fractions of the material obtained at each stage of the chemical treatment. Working on a small scale, a satisfactory method was found of separating the greater part of actinium and ionium from the residues. As the laboratory had no provision for chemical work on the comparatively large scale required, it was arranged that the initial work of concentration should be done by Messrs. Tyrer and Co. at their works, under the direction of Mr. Greenwood. It will be seen that the method applied on the large scale was successful in the separation of the ionium, but did not effect a separation of the actinium at the right point. As activity measurements had been made at each stage of the chemical process it was finally not difficult to locate the position of the actinium, and to affect its partial concentration.

My thanks are due to Mr. Greenwood for his assistance in the initial work of separation, and particularly to Dr. Boltwood for the great trouble he has taken in separating and concentrating the ionium and actinium in the residues.

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The preliminary treatment was carried out at the works of Thomas Tyrer and Co., at Stratford, London, under the direction of Mr. H. C. Greenwood, M.Sc., of this laboratory, and consisted of the following operations :—

The weight of the wet paste was 21·2 kilos. The ignition of a small sample indicated that the proportion of volatile material present was equal to 68 per cent. of the total. The paste was heated with 35 litres of commercial hydrochloric acid, the mixture was boiled down to remove the excess of hydrochloric acid, and the residue was boiled with 100 litres of water. The undissolved materials were allowed to subside, the clear solution was decanted, and the remaining solids were repeatedly treated with hot water until all soluble substances had been removed. The insoluble portion was again treated with hydrochloric acid and with water. The solutions obtained were combined and allowed to cool, when a considerable quantity of lead chloride separated. This was removed, and the solution was treated with an excess of hydrogen sulphide. The precipitated sulphides were filtered off, and the solution, after the addition of about 8 litres of strong nitric acid, was heated to boiling. An excess of ammonia was added to this solution, and the mixture was boiled with steam. After standing over night the precipitated hydroxides were removed by filtration, and the filtrate was evaporated down until a considerable residue of ammonium salts was obtained. This residue will be referred to later as *residue B*. The precipitate of hydroxides was dissolved by warming with dilute hydrochloric acid, and the solution was diluted with water. To this solution was added a solution of 3 kilos. of oxalic acid. Ammonia was also added to neutralise the excess of hydrochloric acid. The mixture was allowed to stand for 17 hours, and the precipitated oxalates were filtered off, dried, and ignited at a low red heat. The oxides obtained in this manner were digested with hydrochloric acid, in which they were almost completely dissolved, and the insoluble material was removed from the solution by filtration. This filtrate, after diluting with water to a total volume of about 20 litres, was nearly neutralised with ammonia, and was then mixed with about 20 litres of a 6-per-cent. solution of hydrogen peroxide. The mixture was allowed to stand over night, and the precipitate which formed was filtered off and dried at 120°. The weight of the dried material was 160 grammes.

All of the materials separated in the course of these operations were carefully preserved. The various solutions obtained were concentrated by evaporation. The activities of the different products were measured immediately after they had been separated, and were further observed at frequent intervals over a period of about nine months.

The various operations described up to this point were all carried out either by, or under the direction of, Prof. Rutherford and Mr. Greenwood. The first material placed at my disposal consisted of the precipitate obtained with hydrogen peroxide. As already stated, this precipitate, when dried, weighed 160 grm. Its activity was about 20 per cent. of the total activity of all the substances which had been separated from the original material. An examination of the records of the different measurements which had been made of the activity of this material from the time of its separation showed that the activity had at first risen by about 20 per cent. and had then fallen to about 65 per cent. of its initial value, after which it had remained approximately constant.

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A preliminary chemical examination of the precipitate indicated that it contained a considerable proportion of rare earths and calcium, but the somewhat surprising observation was made that very considerable amounts of fluorine were also present. It was at first difficult to account for the presence of this element, but from inquiries it was learned that the hydrogen peroxide solution used for the precipitation had been prepared by a process which resulted in its being largely contaminated with hydrofluosilicic acid. Owing to the presence of the fluorine, the decomposition of the precipitate was extremely difficult, but was finally accomplished by heating the material with concentrated sulphuric acid.

The product obtained in this way was extracted with cold water, and the insoluble portions were again heated with sulphuric acid. After this operation had been repeated several times, a solution containing the rare earths, and an inactive residue consisting of calcium sulphate and silica, were obtained. The solution was heated to boiling and an excess of ammonium oxalate was added. The mixture was allowed to stand for 24 hours and the precipitate formed was removed by filtration. This precipitate was dried and converted into the oxides by gentle ignition. The weight of the oxides, which consisted chiefly of cerium and didymium oxides, was about 95 grm. The oxides were dissolved by hydrochloric acid and the rare earths present were precipitated as hydroxides by adding an excess of ammonia. The hydroxides were dissolved in a slight excess of hydrochloric acid. The solution was diluted, heated to boiling, and an excess of sodium thiosulphate was added. The mixture was boiled for some time, and the precipitate which formed was finally filtered off. This precipitate was decomposed by warming with a slight excess of hydrochloric acid, and the precipitation with sodium thiosulphate was repeated. This operation was carried out in all four times, and the precipitate obtained in the last operation was dried and strongly ignited.

The final material obtained in this manner consisted of pure white thorium oxide and weighed 1·8 grm. It was highly radioactive, because of the ionium which it contained, and had an activity about 3000 times that of an equal weight of uranium oxide. Two thin films of this material, one weighing 1·27 mgrm. and the other weighing 0·65 mgrm., were prepared and the number of α-particles emitted by these films were kindly counted for me by Dr. Geiger. According to his measurements, the average number of α-particles emitted by the total quantity of 1·8 grm. of material was $18{\cdot}1 \times 10^7$ α-particles per second. It has been shown by Rutherford and Geiger* that the number of α-particles emitted by 1 grm. of radium is $3{\cdot}4 \times 10^{10}$ per second. The

* 'Roy. Soc. Proc.,' A, 1908, vol. 81, p. 162.

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amount of ionium present with the thorium was therefore equal to the amount in equilibrium with 5·3 mgrm. of radium.

A sample of the original "actinium residues" had been tested and found to contain a considerable proportion of actinium, but very little actinium, if any, had been separated with the "hydrogen peroxide" precipitate which contained the ionium. An effort was therefore made to discover what had become of the actinium. It has been noticed by several observers* that the precipitation of actinium by ammonia is very uncertain and is often quite incomplete. It therefore appeared highly probable that the actinium present in the original "actinium residues" had remained in solution after the treatment with ammonia described on p. 78. The residue of ammonium salts (denoted on p. 78 and below as "residue B") obtained by concentrating the filtrate from the hydroxides precipitated with ammonia was carefully examined. It was found from the records kept that the activity of these salts had at first fallen to about 70 per cent. of its initial value, and had then risen until it was 20 per cent. greater than when the salt was first prepared. This rise in the activity during a period of about six months indicated the presence of some permanent radioactive constituent having chemical properties similar to those of actinium.

The total weight of "residue B" was about eighteen kilogrammes, and, as already stated, it consisted chiefly of chloride and nitrate of ammonium. By fractional recrystallisation the greater proportion of the ammonium salts were separated and were found to be practically free from radioactive constituents. The ammonium salts remaining in the mother liquor were destroyed by continued boiling with a mixture of hydrochloric and nitric acids. The excess of acid was largely removed by evaporation and the residue, consisting chiefly of calcium salts, was dissolved in water and diluted to a volume of about ten litres. This solution was heated to boiling, and a very slight excess of pure ammonium hydroxide was added. A slight precipitate formed and, when the solution had cooled, this was filtered off. It was finally ignited, and weighed about ten grammes.

The material obtained in this manner was only slightly radioactive when first prepared, but its activity increased rapidly and at a rate corresponding to the recovery of activity by an actinium preparation from which the radio-actinium and actinium X have been separated. After about four months its activity was over 20,000 times that of an equal weight of uranium oxide, and it gave off relatively large quantities of actinium emanation. The relative amount of actinium present in this material was

* Hahn, 'Phil. Mag.,' 1907, vol. 13, p. 165; Levin, 'Phys. Zeit.,' 1907, vol. 8, p. 129; Boltwood, 'Am. Journ. Sci.,' 1908, vol. 25, p. 292.

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not accurately determined, but it was roughly estimated to be equivalent to the amount of actinium in equilibrium with 30 mgrm. of radium in a radioactive mineral. A further concentration of the actinium of this material was not attempted.

Production of Helium by Ionium.

A portion of the thorium oxide containing ionium, which was obtained in the chemical operations previously described, was used for determining the production of helium by ionium. The amount of material taken weighed 1·5 grm. This was sealed up with a small quantity of pure oxygen in a tube of Jena "combustion" glass. After a period of 125 days the ionium preparation was heated to a bright red heat, and the gases were pumped out of the tube and collected. The amount of helium present in the gases was then accurately measured, and was found to be 0·031 cu. mm.* The identity of the helium was readily demonstrated by spectroscopic tests.

The number of α-particles emitted by 1·5 grm. of the ionium preparation was $15{\cdot}1 \times 10^7$ per second. This corresponds to the number of α-particles emitted by 0·0045 grm. of radium. Since the production of helium per gramme of radium is 0·107 cu. mm. per day, the amount of helium produced per day by the ionium should be $4{\cdot}75 \times 10^{-4}$ cu. mm. In 125 days the amount would therefore be 0·0595 cu. mm. This is about twice the amount that was actually found, but as no other means than heating was employed for displacing the helium from the solid thorium oxide, the fact that the quantity obtained was smaller than the quantity to be theoretically expected is not in itself significant.

The main result of this investigation was to demonstrate clearly that helium is produced by ionium as well as by other products which emit an α-radiation.

* The method employed and the apparatus used for the determination of the helium will be described elsewhere.

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The Relative Atomic Weights of Nitrogen and Sulphur.

By F. P. Burt and F. L. Usher.

(Communicated by Sir William Ramsay, F.R.S. Received May 26,—Read June 30, 1910.)

(From the Chemical Laboratory, University College, London.)

In 1905, nitrogen sulphide was being prepared and used in large quantities at University College, Bristol, and it was due to a suggestion of Prof. Francis that it might prove a suitable substance for determining the relative atomic weights of its constituent elements, that the present research was undertaken. No direct measurement of the ratio N : S has previously been made, and since the atomic weight of sulphur is still uncertain, a useful step is gained in acquiring an accurate knowledge of that ratio. The compound N_4S_4 has the advantage of containing no other element.

Preparation and Purification of Nitrogen Sulphide.

All the nitrogen sulphide employed in this research was made in Bristol by Prof. Francis and Mr. O. C. M. Davis, by passing dry ammonia into a benzene solution of sulphur chloride. The main products of the reaction are nitrogen sulphide, nitrogen, and hydrogen chloride. The sulphide which was deposited on concentrating the benzene solution contained traces of sulphur. We used as our raw material some sulphide which had stood for many months in the air, and which contained a large proportion of free sulphur as well as ammonium salts. The mixture was extracted with pure dry benzene in a Soxhlet apparatus, and the resulting solution contained all the nitrogen sulphide and relatively little sulphur; on cooling, large needles of nitrogen sulphide were deposited, together with a little finely divided sulphur. The crystals, after being twice washed with cold carbon disulphide, and then with benzene, were powdered on a porous tile and placed in a desiccator containing calcium chloride and cocoanut charcoal.

Prof. Travers suggested that an attempt should be made to analyse the sulphide in such a way as to obtain free nitrogen, which could be measured in a constant volume gas thermometer, and with this end in view it was sought to decompose the substance by heating it *in vacuo*. It was found that at about 80° the sulphide began to volatilise without decomposition, being deposited again as a crystalline sublimate on the cool parts of the vessel. If the sulphide was sublimed *in vacuo* over a roll of silver gauze, tightly packed in a vertical glass tube, decomposition was complete when

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the temperature of the silver was above 200°, though at temperatures between 100° and 120° the vapour was not decomposed to any appreciable extent. This fact at once suggested a satisfactory method of freeing the sulphide from any traces of sulphur. Blank experiments showed that if free sulphur was similarly sublimed *in vacuo* below silver gauze, the silver blackened evenly from below upwards, and no trace of sulphur could be detected on the clean glass above the gauze. The powdered nitrogen sulphide, obtained as described above, was placed in quantities of about 1 gramme in a series of vertical glass tubes which could be exhausted by means of a mercury pump. Above the sulphide in each tube a roll of silver gauze about 5 cm. long was fitted. A steam jacket surrounded each tube up to the level of the top of the silver gauze.* The nitrogen sulphide was then sublimed *in vacuo*, when it was deposited in crystals on the upper cool portions of the tube. From 12 to 24 hours' heating was necessary to sublime 1 grm. of the sulphide. It was noticed that a deep blue transparent film gradually made its appearance on the walls of the sublimation tube some way above the yellow sulphide, and finally crept down to meet the latter if the heating was continued long enough. The probable explanation of this curious phenomenon is discussed by one of us elsewhere.† The blue substance has been shown by analysis to be a sulphide of nitrogen, having the same percentage composition as the ordinary sulphide, but under these conditions it is formed in practically unweighable quantities. During the process of sublimation the silver gauze was superficially coated with sulphide, and a small quantity of nitrogen was pumped off, amounting to a fraction of a cubic centimetre after 12 hours' heating. The traces of gas evolved had an odour of benzene, carbon disulphide, and sulphur dioxide; the last was possibly due to traces of oxygen in the silver, while the others must have been derived from the solvents used. We never succeeded in obtaining nitrogen sulphide that did not yield traces of benzene (or other solvent) on sublimation *in vacuo* unless that nitrogen sulphide had already been sublimed *in vacuo*.

At the end of the experiment the sublimation tubes contained a small white residue, consisting of fragments of filter paper and porous tile. The product obtained by sublimation over silver *in vacuo* consisted of large, orange-coloured crystals, which must necessarily have been free from liquid or gaseous inclusions. When struck, or rapidly heated in air, they detonated violently. Dr. Herbert Smith has kindly examined their crystalline form,

* This was previously heated red-hot in the outer cone of a blow-pipe flame in order to remove oxidisable impurities.

† 'Trans. Chem. Soc.,' 1910, vol. 97, p. 1171.

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and finds that they belong to the monoclinic system. They are therefore of the same type as the crystals deposited from solution, examined by Artini.*

The specific gravity of the sublimed sulphide, which was required in subsequent calculations, was determined by weighing in air and water at 20° in a small specific gravity bottle. We obtained as the result of two determinations the values 2·248 and 2·235, giving a mean of 2·24, sufficiently accurate for a vacuum correction. The specific gravity of the unsublimed sulphide was also determined; we obtained the values 2·21 and 2·19, giving a mean of 2·20, which is in agreement with the results of other observers. Nitrogen sulphide is so slowly hydrolysed by water that it is perfectly safe to use this liquid.

A large number of analyses were carried out by subliming nitrogen sulphide *in vacuo* over silver gauze heated to about 360°. The silver gauze (which was supplied by Messrs. Johnson and Matthey) was freed from oxygen by heating to redness in a stream of hydrogen, and the occluded hydrogen was got rid of by prolonged exhaustion at the same temperature. The gauze was finally exhausted from nitrogen at 360°. As the results obtained were unsatisfactory, the apparatus is not described. There was every reason to believe that the nitrogen sulphide was completely decomposed by the silver; the line of demarcation between the silver sulphide and the unattacked silver was perfectly sharp and definite at the end of a determination; moreover, the cool part of the reaction tube above the silver gauze would have shown the presence of unweighable traces of nitrogen sulphide or sulphur, and the glass was found to be always perfectly clean. We are inclined to attribute the discrepant results to the occlusion of nitrogen by silver sulphide at the moment of its formation. A similar phenomenon has been observed by Dr. R. W. Gray in the reduction of nitric oxide by metallic nickel.† If this is the correct explanation, it would have been necessary to fuse the silver sulphide, which would have involved manipulative difficulties of so serious a nature that we decided to devise some other method of analysis which should dispense with the employment of a metal. Our first attempt was to replace the silver by tightly packed quartz wool, but we found that at 360° the quartz only partially decomposed the nitrogen sulphide.

We finally succeeded by using a quartz reaction tube, in which quartz wool was heated to bright redness by a naked flame.

* 'Zeitschr. für Kryst.,' 1906, vol. 42, p. 68.

† "Über das Atomgewicht des Stickstoffs," Inaug. Dissert., Bonn, 1907.

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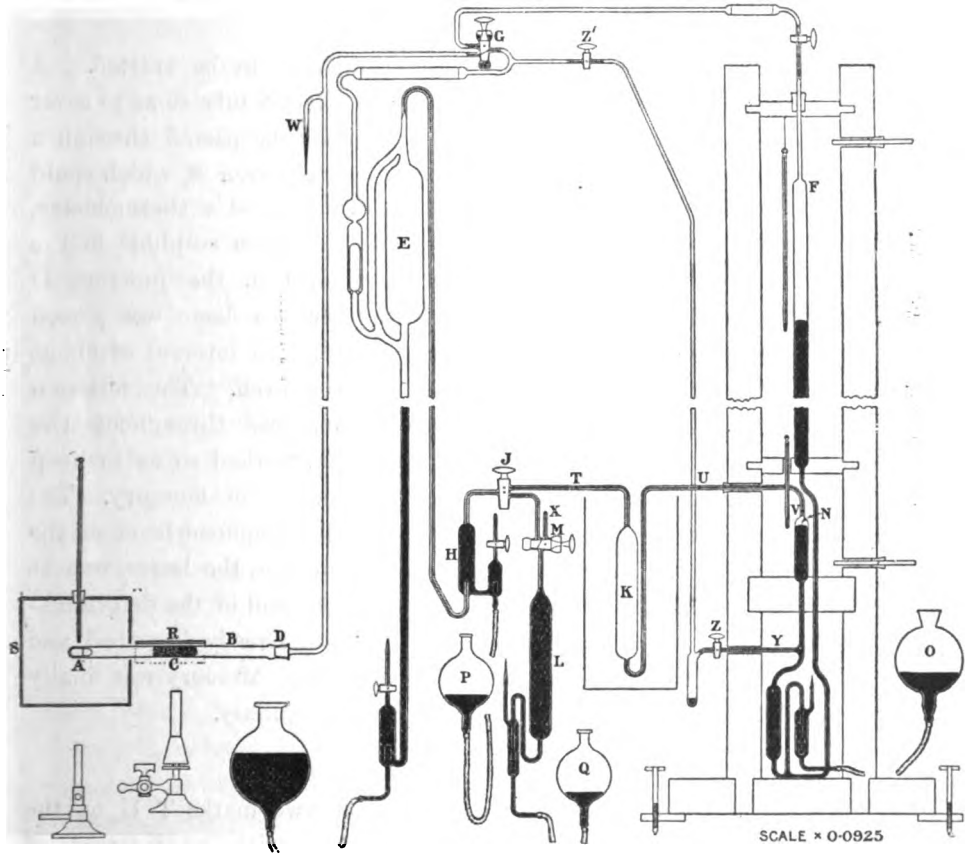
Description of Apparatus and Details of Procedure.

The figure represents the apparatus in which our final analyses were carried out. A weighed quantity of nitrogen sulphide in the small quartz bucket A was placed in the quartz reaction tube B; a plug of quartz wool C, which had been treated in a manner to be subsequently described, was then pushed into the centre of the reaction tube, and the latter was attached to the greased push-join D. The Töpler pump E could be put in communication



either with the reaction tube or with the manometer head F by means of the three-way tap G. The capillary fall tube of the pump was turned up and sealed as an inserted join into the gas collector H. A capillary tube sealed to the upper end of H carried another three-way tap J leading on the one hand to the measuring cylinder K and on the other to the potash tube L, which could also be opened to the air through the third three-way tap M. The measuring cylinder K was connected by means of capillary tubing with the dead space N and manometer F. Before a determination was started

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the dead-space, measuring cylinder, and connecting capillaries, after exhaustion by the pump, were filled with mercury from the reservoir O. The reaction tube was then exhausted, the air being expelled through the collector and potash tube; after exhaustion was complete, any traces of gas sticking at the end of the capillary fall tube or on the walls of H were collected by lowering the reservoir P with the tap J closed, until the mercury in the collector fell to the level of the inserted capillary; the reservoir was then raised again, and any gas collected was expelled into the potash tube L and thence into the air.

The apparatus was now ready for a determination to be started. A ∩-shaped roof of asbestos R was placed over the reaction tube so as to cover the quartz wool, and the last 8 cm. of the reaction tube passed through a closely fitting circular aperture into a cubical asbestos oven S, which could be heated by an ordinary Bunsen burner. The oven carried a thermometer, of which the bulb was in close proximity to the nitrogen sulphide in the tube. A stream of cold water was arranged to drip on the junction D throughout the determination. A large, roaring Bunsen flame was placed under the quartz wool in the reaction tube, and after an interval of about ten minutes the flame was lit under the asbestos oven. The nitrogen sulphide was volatilised at a temperature which rose throughout the determination from 100° to 170°, and the pump was worked so as to keep the average pressure of nitrogen at a few millimetres of mercury. The sulphur was deposited as a lemon-yellow crust in the neighbourhood of the push-join. As soon as the collector H was full of gas, the latter was at once transferred to the measuring cylinder, and, at the end of the determination, the last traces of gas were collected in the way already described, and added to the main quantity in the measuring cylinder. Mercury was finally taken through the tap J and set to a mark T on the capillary.

Measurement of the Nitrogen.

The volume of the measuring cylinder between two marks T, U, on the capillary stem was determined on two occasions with an interval of four years. The earlier calibration was made with water, and the later with mercury; the following are the values obtained—

Calibration with water ... { (i) 105·371 c.c. / (ii) 105·373 „ } Mean = 105·372 c.c.

Calibration with mercury { (i) 105·367 c.c. / (ii) 105·370 „ } Mean = 105·369 c.c.

The agreement obtained was very satisfactory, and since the small difference after a period of four years was within the limits of experimental

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error, the more recent value was adopted. The capillary volume between the marks U and V was calibrated with mercury, and amounted to 0·152 c.c. The lead-glass dead-space, manometer tube, millimetre scale, and the water-bath in which they were set up had already been used by Dr. Gray and one of us in a research on the compressibility of hydrogen chloride.* The volume of the dead-space was 1·275 c.c.

To carry out a measurement of nitrogen, the measuring cylinder K was surrounded by a bath containing powdered ice and water, and the mercury was set exactly to a glass point in the dead-space. The distance between the upper mercury meniscus in the manometer tube and the dead-space point was then determined by means of the scale suspended in the bath, fractions of a millimetre being measured by a telescope provided with a Hilger micrometer eyepiece. For a fuller description of this part of the apparatus, the paper already referred to may be consulted.

The temperature of the mercury column was kept constant by a stream of water circulating through the bath, and was registered by two thermometers, one at the level of the dead-space and the other at the level of the upper meniscus.

In this way the pressure exerted by a known volume of nitrogen at a known temperature was obtained, and in order to calculate its mass a knowledge of the density of the gas was all that was required. We have taken the value 1·2514 grm. as the weight of a litre of nitrogen at 0° and 760 mm. in London. The question of the density of nitrogen is considered at the end of the paper.

The nitrogen sulphide was weighed in a small quartz bucket, provided with a handle so that it could be lifted with a glass hook without contact with the fingers. The weight of the bucket was about half a gramme. It was carefully cleaned by treatment with hot chromic acid and subsequently heating to redness on a platinum wire, and was first weighed empty. A suitable quantity of nitrogen sulphide was then introduced by means of a glass spatula and the bucket was weighed again, and then immediately lowered into the reaction tube.

While the weighings were in progress the reaction tube was cleaned with chromic acid, washed, dried, and finally heated red-hot.

Preparation of the Quartz Wool.

The quartz wool employed was obtained from the Silica Syndicate in the form of a hank of fibres with a mean diameter of about 0·01 mm. It was first of all necessary to "felt" this by hand so as to form a compact plug,

* 'Trans. Chem. Soc.,' 1909, vol. 95, p. 1659.

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and it was found that 3 grm. when so treated occupied a length of about 6 cm. when tightly pressed into the reaction tube. Such a plug was calculated to contain $10\frac{3}{4}$ miles of fibre with a surface of over 5,000 sq. cm. It was realised that so large a surface might involve an appreciable correction for occluded air, and a series of measurements was made to elucidate the question. After the process of "felting," the wool was packed into an open-ended quartz tube—of the same internal diameter as the reaction tube—and heated for several hours to bright redness in a stream of dry air, freed from dust and carbon dioxide, and finally allowed to cool in the air-stream. In this way any carbonaceous matter was oxidised and the wool was never again touched with the fingers.

From the open quartz tube it was pushed into the reaction tube by means of a glass rod. The reaction tube was attached to the pump, exhausted in the cold, and then heated as in an actual analysis. The small quantity of gas evolved was collected and measured in the calibrated capillary at the top of the collector H. When no more gas could be pumped off the tube was allowed to cool and air was admitted through a soda lime tube at the capillary W. The reaction tube was removed and most of the grease in the mouth was wiped off with a clean rag. The tube was then held horizontally and the last traces of grease were burnt out of the neck by heating red-hot with a naked flame in a current of dust-free air. In order to prevent backward diffusion of the products of combustion on to the quartz wool, a piece of quill tubing of silica, which conducted the air current, was pushed well inside the mouth of the tube beyond the heated zone.* As soon as the tube was cold the wool was transferred by the aid of a glass rod bent into the form of a corkscrew to the open-ended quartz tube and the latter was at once put into a desiccator containing potash. In this way the wool underwent precisely the same manipulation and short exposure to the air of the laboratory that were inevitable between two actual analyses. Two more blank experiments were made with the same wool in exactly the same manner as just described. The volumes of air obtained in the three cases were:—

(i) 0·0173 c.c. (ii) 0·0099 c.c. (iii) 0·0056 c.c.

The diminution in the volume of occluded air was due partly to a small mechanical loss of wool, occasioned in transference, and partly, perhaps, to a decrease in its occluding power, owing to the prolonged heating.

* After an analysis of nitrogen sulphide the mouth of the reaction tube contained not only grease but sulphur, and this was burnt out with the grease in the manner described. In order to keep the conditions as similar as possible, a piece of sulphur was placed in the neck of the reaction tube and burnt out with the grease in "occlusion" experiments, on occasions when a sublimate was not already present.

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If the volumes of air obtained are plotted against the ordinal numbers of the experiment, the three points lie very nearly on a straight line. In any series of analyses, therefore, it was only necessary to make two occlusion measurements, one at either end of the series, and to use a straight line interpolation for fixing the correction to be applied to the intermediate determinations. It was found inconvenient in practice to start any series of experiments with a plug of quartz wool occupying a greater length than 6 to 7 cm. of the reaction tube, and this quantity only sufficed for about six experiments (whether occlusion measurements or analyses) partly because of the small constant loss, and partly because the continued heating and manipulation rendered the wool inelastic and powdery, when it would no longer form a tight plug in the reaction tube.

It will probably be conceded that no more air, that is, oxygen and nitrogen, would be washed out of the hot wool when nitrogen sulphide was being sublimed over it than would be pumped off by exhaustion *in vacuo* at the same temperature, though this would not be true for any denser gases which might find access to the wool. Of such gases, the only two which could possibly have reached a significant concentration in the room in which we worked were carbon dioxide and sulphur dioxide,* and since it was impossible to avoid exposing the wool to the laboratory air for a short period between each experiment, it was essential to investigate the possibility of quantitative error from this source.

We may state at once that, so long as the wool was exposed to the laboratory air for indeterminate periods, we failed to obtain constant results for the N : S ratios, even when the necessary correction was made for occluded air, but it was subsequently discovered that if the nitrogen volumes in a series of determinations were treated with moist potash and then dried, a contraction occurred, which at once brought the ratio to a constant value. The results of a large number of our earlier determinations might have been corrected, had we at that time suspected the presence of traces of gas absorbable by potash.

A point still to be considered was whether the air pumped off the hot wool *in vacuo* contained any gas absorbable by potash. Since two separate corrections were made on the nitrogen, namely, that for air, which was fixed by the occlusion experiments, and that for carbon dioxide or sulphur dioxide, which was determined by measuring the contraction of the nitrogen on treatment with potash, the total correction would have been too large if any carbon dioxide had been measured as occluded air. By exposing the

* Neither ammonia nor water vapour need be considered, as both would be removed by the phosphorus pentoxide between the reaction tube and the pump.

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minute quantities of gas obtained in the occlusion experiments to potash, and then remeasuring them, a very small contraction of the order of 1 cu. mm. was observed. This could be neglected without appreciable error.

At an early stage in our experiments with a quartz reaction tube, it was discovered that a small quantity of hydrogen from the flame passed through the hot quartz; moreover, when a similar flame was used, the quantities of hydrogen that entered the tube in unit time were remarkably constant. This conclusion was arrived at in two different ways, and was repeatedly confirmed. In the first place, it was noticed that it was impossible to pump the heated tube "tight," gas continuing to collect in the pump at the rate of about 3·5 cu. mm. per hour. In order to apply a direct test for hydrogen, the gas obtained in a particular occlusion experiment was mixed with a little additional air, and transferred to a small gas burette provided with platinum electrodes. On passing a spark a contraction occurred:—

	Volume before sparking	= 0·065 c.c.
	Volume after sparking	= 0·046 „
	Contraction	= 0·019 „
Therefore	Volume of hydrogen	= $0·019 \times \frac{2}{3}$ = 0·013 c.c. in $3\frac{3}{4}$ hours
		= 0·0036 c.c. per hour.

Values obtained by direct measurement of the constant quantity of gas, collected when the empty tube was heated, varied from 0·0033 to 0·0040 c.c. per hour.

For correcting our nitrogen volumes, we assumed the hydrogen to enter at the rate of 0·0036 c.c. per hour.

Treatment of Nitrogen with Potash.

After the initial measurement of nitrogen, the gas was taken, *viâ* the collector, into the tube L. This tube had been prepared before it was set up, by melting a stick of caustic potash in it, and rotating it so as to cover the walls with a film of the fused alkali. Before letting in the nitrogen, the mercury in L was taken down to the bottom of the tube, with the tap M closed, by lowering the reservoir Q; any bubbles of gas caught in the potash film escaped into the vacuum so produced, and were collected and expelled into the air, when the mercury was taken up again. This operation was always carried out twice. A thread of water (30 or 40 cu. mm.) was now introduced through the capillary tube X, so as to moisten the potash, and the nitrogen was then transferred to L. After standing over-night, the nitrogen was returned to the measuring cylinder, again with the same precaution of lowering the mercury, so as to obtain the last traces, and the

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mercury in the dead-space was taken below the level of the side-tube Y. By an alternate manipulation of the taps Z and Z′, the gas was cautiously taken into the pump until the pressure in the measuring cylinder was reduced to a few centimetres of mercury. Keeping the taps Z and Z′ open, a stroke of the pump was taken, so as to fill the collector H; the tap J was then opened, so that gas flowed from the collector to the measuring cylinder, and thence over the phosphorus pentoxide back into the pump chamber. About 30 strokes were taken, so as to dry thoroughly not only the gas, but also the glass walls of the collector, measuring cylinder, and dead-space. When this was accomplished mercury was allowed to rise in the dead-space, and seal the tap Z, which was then turned off. The rest of the nitrogen was then returned to the measuring cylinder, by working the pump till exhaustion was complete; the last traces were collected by lowering the reservoir P, and the mercury was set again to the mark T on the capillary. A second measurement of the nitrogen was then made. We found that the operation of circulating the gas through the system could be carried out without gain or loss; on repeating the whole process with a quantity of nitrogen which had already been treated with potash and dried, we recovered the original volume to within 1 part in 50,000.

In the two series of experiments of which the results are given in the following table, the quartz wool was treated in a precisely similar way. The addition of the potash tube to the apparatus was made between the two series, so that the actual contraction of the nitrogen on treatment with potash was only measured in the second series. Since, however, the ratios from Experiments 2B and 3B were in good agreement respectively before and after the gas had been treated with potash, and since, further, the uncorrected results of Experiments 2A, 3A, and 4A agreed with each other, and with the uncorrected results of 2B and 3B, we applied the correction determined in these two cases to the corresponding experiments in series A. Again, since the corrected result of Experiment 1B agreed with the corrected results of 2B and 3B, the same contraction correction actually determined in the case of 1B was applied to 1A.

In every series of analyses with a given specimen of quartz wool, the value from the first experiment was always higher than the values from the succeeding ones. This was apparently due to the presence of a larger proportion of gas absorbable by potash, as indicated by the contraction measured in Experiment 1B. When the history of the wool and the time of its exposure to laboratory air had also been the same, as in the two series given, the values from the first experiments also agreed very closely. The values obtained from the second, third, and sometimes the fourth

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Table of Results.

No. of experiment.	Nitrogen sulphide.	Vacuum correction.	Pressure of gas.	Volume at N.T.P.	Correction for hydrogen.	Occluded air.	Gas removed by potash.	Corrected volume.	Density at observed pressure.	Weight of nitrogen.	Weight of sulphur by difference.	Ratio, N/S.
	grm.	mgrm.	mm.	c.c.	c.c.	c.c.	c.c.	c.c.		grm.	grm.	
1A	0·469455	0·258	812·73	114·162	0·013	0·019	0·084	114·046	1·25148	0·142726	0·326729	0·43685
2A	0·442787	0·243	766·18	107·624	0·012	0·017	0·018	107·578	1·25144	0·134627	0·308160	0·43688
3A	0·456326	0·249	789·50	110·902	0·011	0·014	0·018	110·859	1·25146	0·138736	0·317590	0·43684
4A	0·470072	0·258	813·29	114·240	0·010	0·012	0·018	114·200	1·25148	0·142919	0·327153	0·43686
1B	0·466918	0·252	808·41	113·550	0·010	0·014	0·084	113·442	1·25147	0·141969	0·324949	0·43690
2B	0·491307	0·261	850·07	119·404	0·012	0·013	0·018	119·361	1·25150	0·149380	0·341927	0·43688
3B	0·484307	0·265	837·97	117·704	0·011	0·011	0·018	117·664	1·25150	0·147257	0·337050	0·43690
											Mean N/S.....	0·43687
											Probable error	±0·000006

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experiment in a series, were nearly constant. Following these constant results came a much lower value, suggesting that some of the nitrogen sulphide had escaped decomposition, because of the diminution in quantity and efficiency of the quartz wool. As a matter of fact, a low value could always be foretold, before the nitrogen was measured, by the appearance of the sulphur sublimate. As long as decomposition was complete, the sulphur solidified at once on cooling, and the colour of the sublimate was a pale lemon-yellow; if, on the other hand, complete resolution of the nitrogen sulphide into its elements had not been effected, the sulphur did not solidify quickly on cooling, and eventually exhibited darker patches of a red or brown colour.

A glance at the table on p. 92 will show that the three separate corrections made on the volumes are very small compared with the total nitrogen volumes; moreover, the probable error on the correction itself is in each case very small. In the case of the hydrogen, the experiments already cited indicate the order of this error to be less than a cubic millimetre for three hours heating, which was the average time occupied by a determination. The largest correction for occluded air is less than 1/6000 of the total nitrogen volume, and the probable error on the correction itself is not greater than 5 per cent.

Finally, the validity of applying a similar contraction correction in cases where it was not actually measured, is supported by many preliminary experiments which showed that quartz wool will take up from the air condensible gases in amount depending almost entirely on the time of exposure, and also by the very good agreement of the ratios among each other before this correction was made.

The agreement already referred to between the constant values on the one hand and the high initial values on the other is evident from the following list of ratios uncorrected for gases absorbed by potash:—

Experiment	1A.	1B.	2A.	3A.	4A.	2B.	3B.
Ratio N/S	0·43735	0·43740	0·43698	0·43695	0·43696	0·43699	0·43701

The following is a full calculation from the data in Experiment 1B:—

Weight of bucket+nitrogen sulphide	1·032683	grm.
Weight of bucket	0·566017	„
Weight of nitrogen sulphide	0·466666	„
Vacuum correction (17° and 758 mm.)	+0·000252	„
Corrected weight of nitrogen sulphide	0·466918	„

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Nitrogen reading :—

Volume of measuring cylinder at 0°	105·369 c.c.
Volume of dead-space, 1·275 c.c.	
Temperature of gas in dead-space, 8°·83	
Volume of gas in dead-space at 0° $= \frac{1{\cdot}275 \times 273}{281{\cdot}83} =$	1·235 „
Volume of intermediate capillary, 0·152 c.c.	
Volume of gas in intermediate capillary at 0° $= \frac{0{\cdot}152 \times 273}{281{\cdot}8} =$	0·142 „
Total volume at 0° and at observed pressure.....	106·751 „

Pressure measurement :—

	Micrometer readings.	Millimetres.	Scale readings
Distance from meniscus set to point in dead-space to scale-line 1 above it	84, 84, 84, 84, 85, 85 : mean 84·33	0·654	0·346 mm.
Distance of upper meniscus below scale-line 815	636, 634, 636, 635 : mean 635·25	4·924	810·076 „

Uncorrected manometric height, 810·076 − 0·346 = ...	809·730 „
Correction for scale errors	+ 0·034 „
Contraction of scale from 16° to 8°·9 (= 7·1 × 0·000009 × 810)	− 0·052 „
Correction of observed manometric height from 8°·88 to 0°	− 1·307 „
Corrected pressure.....	808·405 „
Volume of nitrogen at N.T.P. $= \frac{106{\cdot}751 \times 808{\cdot}405}{760} =$	113·550 c.c.
Correction for hydrogen.....	− 0·010 „
Correction for occluded air.....	− 0·014 „
Contraction on treatment with potash.....	− 0·084 „
Corrected volume of nitrogen at N.T.P.	113·442 „

Density at observed pressure = 1·25144 × 1·000027 = 1·25147

∴ Weight of nitrogen = 113·442 × 0·00125147 = 0·141969 grm.
Weight of nitrogen sulphide taken ..... = 0·466918 „
Weight of sulphur by difference ..... = 0·324949 „
Ratio N/S = 0·436897 „

Discussion of Errors.—The question of the purity of the nitrogen sulphide has already been considered. With regard to its stability in dry air we may remark that no change in weight in a specimen was detectable after several days' standing in a desiccator; moreover, it was found to be immaterial as regards the resulting ratio, whether we used nitrogen sulphide just removed from a sublimation tube, or crystals that had been kept for several days in dry air. In order to ascertain whether there was any danger of losing nitrogen sulphide by volatilisation during the preliminary exhaustion of the reaction tube at the room temperature, a weighed quantity of the finely divided substance contained in a quartz bucket was sealed up in a glass tube, which was then exhausted and left for an hour. No loss in weight

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could be detected, and was certainly less than 0·000005 grm.; any loss, therefore, during the half hour required for the preliminary exhaustion must have been quite negligible.

Weighings.—The weighings were made on an Oertling's assay balance carrying a maximum load of 2 grm. Each arm of the beam was divided into 50 parts, and fractions of a milligramme were estimated with a milligramme aluminium rider. The sensibility of the balance for the loads used was about six pointer-scale divisions per 0·1 mgrm., and an accuracy of five in the sixth place (1 in 80,000 on the nitrogen sulphide) was probably attained. The pointer oscillations were read with a lens, tenths of a division being estimated by eye. In weighing nitrogen sulphide we used the platinum weights alone of the same set with which the measuring cylinder was calibrated. By using weights of the same set for both operations, any small error due to deviation of the weights from their absolute face values was, of course, eliminated. The weights were calibrated against each other in air, using another set as counterpoises, according to the method of Richards. Vacuum corrections were applied to the apparent weights of nitrogen sulphide, and of water or mercury used to calibrate the measuring cylinder, but not to the brass and platinum weights themselves, since absolute values were not required.

Accuracy of Nitrogen Measurement.—The calibration of the constant volume has been discussed already. In order to see whether there was an appreciable change of volume of the measuring cylinder as the internal pressure changed, the exhausted cylinder was filled with mercury to a mark on the capillary. Air was then admitted into the dead-space, and the movement of the capillary meniscus observed as the internal pressure rose. It was found that the cylinder expanded by 0·002 c.c. for a rise of pressure of 300 mm. Since in our experiments the pressure of the nitrogen never differed from the atmospheric pressure by more than 100 mm., this source of error could be neglected.

That the volume of the measuring cylinder was not altered by distortion when filled with mercury was proved by observing the behaviour of the meniscus in the capillary when the whole cylinder was immersed in mercury; the change, if any, was not greater than 0·0002 c.c.

The two thermometers in the manometer bath were previously compared with a standard thermometer at 0°, and at 8°·8, which was about the usual temperature of the water. In correcting the volume of gas in the dead-space to 0° we used the coefficient 1/273; this was quite accurate enough, as the volume to be corrected was only 1·275 c.c. It was only necessary to know the temperature of the gas in the intermediate capillary to within 5°.

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Accuracy of Pressure Measurement.—Since the accuracy of the pressure measurements made in this particular apparatus has already been fully discussed,* it is unnecessary to examine it again here. We believe that the corrected pressure of the gas was known to within 0·02 mm., which corresponds with an error of 1 in 28,000 on the N/S ratio.

The Density of Nitrogen.—Guye,† discussing the results obtained by Rayleigh and Ramsay, Leduc, and Gray, arrived at the value 1·2507 grm. for the weight of a "normal litre" of nitrogen. On correction to the latitude of London this becomes $1{\cdot}2507 \times 1{\cdot}000588 = 1{\cdot}25144$.

Using the value obtained by Chappuis for the compressibility coefficient between 1 and 2 atmospheres, namely, −0·00043, we have applied a small correction where the observed pressure differed appreciably from 1 atmosphere.

Atomic Weight Discussion.—The long debated question as to whether the atomic weight of nitrogen was more accurately represented by the number 14·04 or 14·01 has now been generally agreed upon, and the lower value, 14·01, which has been adopted by the International Commission, may be taken as a very close approximation to the true atomic weight. The subject has been exhaustively discussed by Guye,‡ by Gray,§ and by Brauner,‖ and the balance of evidence seems in favour of a value very slightly lower than 14·01.

As regards the atomic weight of sulphur, later researches have yielded results not very different from Stas's value 32·06. From the results obtained by Richards and Jones¶ on converting silver sulphate into silver chloride, an atomic weight of sulphur can be calculated, but it depends on the value of chlorine, and, unfortunately, a small variation in the value adopted for chlorine involves a large difference in the resulting value for sulphur. Thus, if Cl = 35·457, S = 32·070; whereas if Cl = 35·460, S = 32·078. The values arrived at by physical methods vary from 32·050 to 32·070. Guye,** by reducing the critical constants of sulphur dioxide, obtained the value 32·065, taking the density as 2·9266 grm. per "normal litre," and Baume and Perrot,†† adopting the same procedure with hydrogen sulphide, obtained the value 32·070, taking the density of this gas as 1·5392

* Gray and Burt, *loc. cit.*

† 'Journ. Chim. Phys.,' 1907, [5], p. 217.

‡ 'Bull. Soc. Chim.,' 1905, [iii], pp. 33—34, 44.

§ "Über das Atomgewicht des Stickstoffs," Inaug. Dissert., Bonn, 1905.

‖ 'Abegg's Handbuch der anorganischen Chemie,' vol. 3, [iii], p. 34.

¶ 'Journ. Amer. Chem. Soc.,' vol. 29, p. 826.

** 'Comptes Rendus,' 1905, vol. 140, p. 1241.

†† 'Journ. de Chim. Phys.,' 1908, vol. 6, p. 610.

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and the atomic weight of hydrogen as 1·00775. D. Berthelot,* calculating the limiting density of sulphur dioxide from the compressibility measurements of Leduc, and of Guye and his colleagues, deduced from the results of the former an atomic weight S = 32·050, and from those of the latter, S = 32·064. There is reason to believe that the form of the *pv* isothermal of a readily condensible gas, such as sulphur dioxide, can be accurately determined only by making a large number of different pressure and corresponding volume measurements, and that attempts to extrapolate from two or three points by means of a parabolic formula or by the application of Van der Waal's equation are not entirely satisfactory.†

We were unable to find any direct check on our N/S ratio in atomic weight literature, but an instructive comparison was obtained by examining some of the results of Richards and his colleagues. From the equations :—

$$AgCl/Ag = 1{\cdot}32867,\ddagger\quad AgNO_3/Ag = 1{\cdot}57479,\S\quad \text{and}$$
$$2AgCl/Ag_2SO_4 = 0{\cdot}91933,\|$$

we obtained by eliminating silver and chlorine the simple relationship

$$(S+64)/(2N+96) = 0{\cdot}774648.$$

By assigning a definite value to either nitrogen or sulphur, the ratio N/S can be calculated, and this ratio is scarcely affected by any probable alteration of the atomic weight of nitrogen. For example, if N=14·010, N/S becomes 0·43683, whereas if N=14·009, the ratio becomes 0·43682. The agreement between these numbers and our own (0·43687) is all the more surprising when one considers the very indirect process by which the former was calculated. From Richards' results sulphur becomes 32·070 if N = 14·009, whilst our ratio makes S = 32·067 to the same standard.

We suggest that some indirect evidence for an atomic weight of sulphur slightly lower than 32·070 is afforded in the recent paper by Thorpe and Francis¶ on the atomic weight of strontium. From a determination of the ratios $SrCl_2/2Ag$, $SrCl_2/2AgCl$, $SrBr_2/2Ag$, $SrBr_2/2AgBr$, $SrCl_2/SrSO_4$, and $SrBr_2/SrSO_4$, the authors obtain six values for the atomic weight of strontium, namely, 87·638, 87·646, 87·645, 87·653, 87·661, and 87·629, when Ag = 107·880, Cl = 35·460, Br = 79·916, O = 16, and S = 32·07. Now the excellent agreement in the first four values is apparently not quite so well maintained in the last two. Out of curiosity, the mean atomic weight of

* 'Comptes Rendus,' 1907, vol. 144, p. 269.
† Gray and Burt, *loc. cit.*, p. 1660.
‡ 'J. Amer. Chem. Soc.,' 1905, vol. 27, p. 525.
§ *Ibid.*, 1907, vol. 29, p. 826.
‖ *Ibid.*, 1907, vol. 29, p. 844.
¶ 'Roy. Soc. Proc.,' A, vol. 83, p. 287.

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strontium obtained from the first four ratios, namely 87·646, was inserted in the last two equations, and the corresponding values for sulphur were calculated. These proved to be 32·068 and 32·066 respectively. Then, starting with the mean of these two, namely, 32·067, and keeping the same values as before for the other elements, the atomic weight of strontium was recalculated from the last two equations. The values obtained were 87·641 and 87·640, which show an excellent agreement with each other as well as with the mean from the first four ratios, 87·646.

On the assumption that our ratio $N/S = 0{\cdot}43687$ is correct, we may conclude that if $14{\cdot}009 \pm 0{\cdot}001$ be the number assigned to nitrogen the atomic weight of sulphur may be taken as $32{\cdot}067 \pm 0{\cdot}002$.

All the preliminary work in this investigation was carried out at University College, Bristol, and we desire to express our thanks to Dr. Morris W. Travers for his invaluable help and suggestions, and for the continued interest which he took in the research; to Prof. Francis, who not only was personally responsible for much of the earlier experimental work, but who also afforded us every facility in the prosecution of the research during this period; and to Mr. O. C. M. Davis, for preparing most of the nitrogen sulphide. We have also to acknowledge a grant from the Chemical Society, which defrayed the expenses of the earlier part of the work. The later part, including the analyses with quartz wool, was carried out at University College, London, and we wish to thank Sir William Ramsay for his interest and encouragement. Finally, we are indebted to Dr. R. W. Gray for his courtesy in placing at our disposal much of the apparatus used.

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UNIV. OF CALIFORNIA

The Production and Properties of Soft Röntgen Radiation.

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(Communicated by Sir J. J. Thomson, F.R.S. Received January 20,—Read February 16, 1911.)

There is a class of problem of the greatest interest in connection with primary Röntgen rays, which as yet has received but little attention from experimental investigators. The kind of problem referred to is indicated by the following two leading questions:—

(1) How do the properties of Röntgen radiation depend on the velocity of the parent cathode rays?

(2) How do the properties of Röntgen radiation depend on the nature of the anticathode used to arrest the motion of the parent cathode rays?

The present communication has to do with soft Röntgen radiation such as is produced in a discharge tube working at only a few thousand volts. The only investigator who appears to have worked with such rays is W. Seitz, and his experiments are referred to later. As a preliminary it will be convenient to present a general view of the ground which will be covered, and to indicate broadly the method employed.

In the present experiments slow cathode rays of known velocity were directed on to one of a series of metallic anticathodes, the Röntgen rays so produced being led out into the open air through an aluminium window, and there tested. The tests applied to the rays were quantitative measurements of:—

(1) Their energy, as indicated by the ionisation produced in a definite thickness of air; (2) their penetrating powers, as indicated by the values of their absorption coefficients in different materials; and qualitative observations on (3) their power of producing corpuscular emission when incident on metal surfaces.

These three properties of Röntgen rays were chosen as being the most important, and the most easily observed. The first two are especially important, since a pulse radiation is sufficiently defined for some purposes by a knowledge of its energy and absorption coefficients. A preliminary account of the work was given in August of last year to the Cambridge Philosophical Society.*

* Whiddington, 'Proc. Camb. Phil. Soc.,' vol. 15, Part VI, p. 574.

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This paper is divided into the following sections:—

§ 1. A description of the apparatus.

§ 2. A theory of the influence of the aluminium window on the constitution of the emerging Röntgen radiation.

§ 3. The dependence of the *energy* of Röntgen radiation—

(*a*) On the nature of the anticathode.

(*b*) On the velocity of the parent cathode rays.

§ 4. The dependence of the *absorption coefficients* of Röntgen radiation—

(*a*) On the nature of the anticathode.

(*b*) On the velocity of the parent cathode rays.

§ 5. The *corpuscular radiation* excited by the incidence of Röntgen radiation on metallic surfaces.

§ 6. Summary and conclusions.

§ 2 occupies the place it does because the theory there advanced makes it much easier to remember the somewhat complicated and otherwise disconnected results of §§ 3 and 4.

§ 1. The Apparatus.

The apparatus can be described conveniently under two main headings: (1) That part of it which generated the radiation, *i.e.* the discharge tube; (2) That part which tested the rays, *i.e.* the ionisation chamber and its connections.

(1) *The Discharge Tube.* (Fig. 1.)—The discharge tube consisted of a tube 65 cm. long and 4 cm. in diameter (its length being at right angles to the

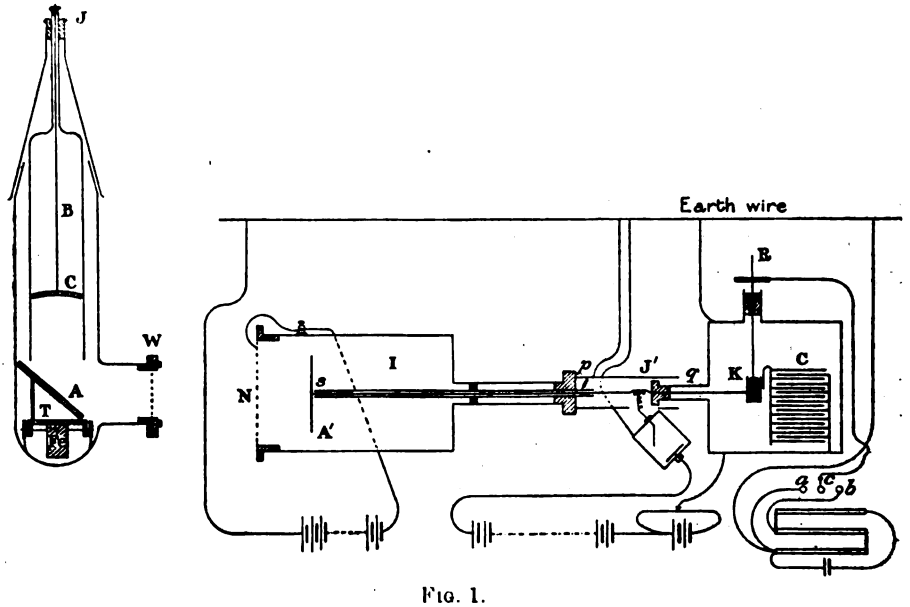

Fig. 1.

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plane of the figure), along the bottom of which aluminium rails were laid down. This tube was fused to two slightly narrower and much shorter side tubes in the manner indicated in the figure. The horizontal one was 5 cm long, terminating with a thin aluminium window; the vertical one was about 30 cm. long, ending in a ground-glass joint. The plane containing these two tubes was at right angles to the length of the long tube. An aluminium carriage T ran on wheels along the track already referred to. This carriage carried a row of anticathodes of various materials, all inclined at about 45° to the horizontal. The materials used were Ag, Al, Sb, Cu, Fe, Ni, Pb, Pt, Sn, Zn. Their surfaces were ground smooth and finally polished with jeweller's rouge. The carriage T was magnetically controlled from outside by means of an electro-magnet and a bar of soft iron mounted under the carriage. The upper flange of the ground-glass joint J carried a tube B, enclosing a concave cathode C mounted at a convenient distance from the carriage. The joints at J were made tight with sealing wax.

The tube B, which fitted very tightly round the cathode C, served two purposes: firstly, it prevented the cathode from sputtering on the walls of the outer tube, and secondly, it helped to concentrate the cathode stream down the centre of the tube. It was found to be extremely important for quantitative work to prevent sputtering on the outer tube, since when it becomes conducting the beam of cathode rays is irregularly attracted to the walls owing to spasmodic induction effects.

The parallel beam of cathode rays striking an anticathode A produce Röntgen rays,* some of which pass down the horizontal tube and emerge through the window W.

The window consisted of a thin sheet of aluminium foil (0·002 cm. thick) supported on a coarse brass-wire grid. The grid was mounted on a heavy brass flange which was waxed on to the end of the horizontal tube. A brass annulus could be screwed down tightly on this flange, thus gripping the foil and making all air-tight. The tube was in direct communication with a Töpler mercury pump and a charcoal liquid-air tube.

In all experiments the anticathode system, consisting of rails and carriage, was connected to earth and made the anode. The window could either be earthed or charged to a potential, as occasion required. The experiments described below were carried out with potentials between the cathode and anode of the tube† up to 3600 volts. The potential up to this point was

* If the potential generating the cathode rays is say 2000 volts, and the anticathode is Pb, then the emerging radiation will for convenience be termed the 2000 volt radiation from Pb.

† Hereafter referred to as "the generating potential."

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obtained from a battery of small accumulators. The high potential was connected to the tube in series with a high voltage key, a milliampère meter and a variable liquid rheostat (copper sulphate in water). The milliampère meter was a Weston instrument, each division being equivalent to 1/10 milliampère. The variable liquid rheostat was operated from a distance by a cord passing over pulleys, and gave a control of about 200 volts on the tube. The potential across the tube (*i.e.* between the anode and the cathode) was measured by a Braun electrometer, with a scale which could be read to 20 volts between 500 and 3500 volts.

Now it is well known that the cathode rays produced by a steady discharge from cells are homogeneous as regards their velocity, which is approximately given by the relation

$$2e/m \,.\, \mathrm{V} = v^2,$$

where

e/m = the universal charge to mass ratio (E.M. units),

v = the velocity of the cathode rays,

V = the potential in E.M. units applied to the terminals of the tube, *i.e.* the reading of the voltmeter $\times 10^8$.

Thus the reading of the voltmeter, multiplied by $2e/m \times 10^8$, gives approximately the square of the velocity of the cathode rays within the tube.

The vacuum in the tube was initially adjusted by use of the Töpler to give a current of 0·2 milliampère at approximately the required potential, the final adjustment being made with the liquid resistance. During the course of a long run the potential across the tube would gradually fall, indicated rather by a diminution in the intensity of the emergent Röntgen rays than by the reading of the electrometer. This was due to the liberation of electrode-gas, which could be absorbed by turning on the charcoal-tube tap for a few moments. After a few months' use, however, this effect became extremely small.

(2) *The Ionisation Chamber and its Connections.*—The ionisation chamber I (fig. 1) was a cylinder of brass, fitted with a detachable gauze front N. Both the gauze and the case of the chamber were usually charged to a saturating potential. To obviate the leakage of charge from the case to the insulated electrode A′, the wire support was encased in and insulated from a brass sheath tube S kept permanently connected to earth. This arrangement somewhat increased the electric capacity of the measuring system, but not to any serious amount. This sheath tube had the additional and very great advantage of completely protecting the insulation which really mattered,

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and this insulation once put in and enclosed in this way remained good almost indefinitely.

The electrode A′ was connected to a mercury key K, enclosed in an earthed box containing a capacity C which could be added to the insulated system in connection with the gold leaf and thus diminish the sensibility. It was necessary in some experiments to adjust rapidly the distance of the gauze N from the window W. For this reason the whole measuring system—chamber, key, and electroscope—were mounted together on a rigid movable platform. It was then easy to move the whole system relative to the X-ray tube. Ebonite insulation was used throughout, and except in very damp weather proved very satisfactory. The absorbing screens had of necessity to be extremely thin, on account of the very low penetrating power of the rays dealt with. The thinnest obtainable leaf was used. The thicknesses were obtained by weighing. The screens were mounted on metal frames fixed to a geometrical slide, the whole being earthed. The geometrical slide enabled any required screen to be inserted with a minimum of delay. This time-saving device was found to be necessary, since it was not often that the tube would run steadily for long at a time.

§ 2. A Theory of the Influence of the Aluminium Window on the Constitution of the Emerging Röntgen Rays.

The experiments described in §§ 3 and 4 are so diverse in their nature and apparently so disconnected that it seems advisable to precede the experimental results by a theory which welds them together, and so aids the memory. This is the only excuse for presenting the following theory here instead of later, and it is to be regarded as tentative, since its simplicity must needs suffer should factors like selective transmission and so on be taken into consideration.

It is well known that many metals can be made to give out characteristic secondary radiation when stimulated by a suitable primary beam. The distinguishing feature of a characteristic radiation, according to Barkla, is its individuality. The quantity may depend on circumstances, but never the quality. It is, however, only when the primary beam contains a constituent more penetrating than the characteristic to be excited that the stimulation can be effected. This law governing the emission of characteristic radiations, in fact, is closely analogous to that law found by Stokes to be true in cases of light fluorescence. The recent researches of Prof. R. W. Wood, however, have shown that there are cases of light fluorescence in which Stokes's law is flagrantly disobeyed.

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The possibility of similar exceptions to the parallel law of characteristic radiation or Röntgen ray fluorescence is indicated by the easy explanation on such an hypothesis of the otherwise hardly explicable results in connection with aluminium described in this paper. The basal assumption is this, that aluminium is capable of emitting a characteristic radiation which may be more penetrating than the exciting primary. Put in other words, it is assumed that Al is an exception to Stokes's law as applied to Röntgen ray fluorescence.

We will now consider what, on such an hypothesis, will be the state of affairs on the emergent side of a plate of aluminium (such as the window of the discharge tube) on which a beam of Röntgen rays is incident.

If the rays are excessively soft, their intensity on the emergent side will be very small—let us suppose inappreciable. Now imagine the incident primary beam to become gradually more penetrating while keeping its energy constant. Then, if the Al emit no secondary rays, there will come a stage (α), corresponding to a penetrating power P_C of the primary rays, when the emergent radiation becomes just strong enough to be detected. But it is conceivable that if the Al were to emit a secondary radiation of greater penetrating power than P_C, radiation might escape from the emergent side of the plate even if the incident primary rays possessed a penetrating power less than P_C.

This would happen if $P_{AL} > P_C$, where P_{AL} is the penetrating power of the characteristic Al radiation, P_C is the penetrating power corresponding to that quality of incident beam, which, in the absence of secondary effects, would just emerge in measurable quantity. The condition $P_{AL} > P_C$ involves the violation of the "Röntgen ray fluorescence" law referred to above.

In the apparatus shown in fig. 1 it will be seen that the Röntgen radiation produced by the incidence of the cathode stream on the target A must pass through the Al window W before reaching the testing vessel I.

The above considerations show that it is not impossible, with certain assumptions, for radiation to be detected by the vessel I even if the primary radiation from A is too absorbable to penetrate the window. As a sort of corollary it would follow that up to a certain limit of generating potential the quality of the emerging radiation would be constant; that is, the penetrating power of the emergent Röntgen radiation would remain apparently constant and independent of the velocity of the cathode rays striking the target (see fig. 7).

It is now necessary to consider some other and more complicated consequences of a violation of the "fluorescence law." There will be no further assumptions made, but it will be necessary to anticipate some of the simpler experimental results of §§ 3 and 4.

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(1) The materials experimented with can be assigned positions in one of two classes according to their power or inability of emitting secondary Röntgen radiations. Group A, which includes Al, contains those anticathodes which emit secondary radiations, while Group B—the larger class—contains those which do not. This is a purely experimental classification.

Metals of Group A when subjected to a beam of cathode rays, and so to a beam of primary Röntgen rays, are imagined to be capable of emitting characteristic radiations of the type conceived above; whereas metals falling into Group B are supposed to emit no secondary radiation when placed under similar conditions.

(2) Experimental analysis of the radiations from members of Group B shows that they are all of the same quality at the same generating potential, but that their penetrating powers increase with the generating potential.

So much for the experimental results which it is necessary to anticipate for the purposes of the following considerations. Consider, first, the constitution of the radiation from a representative anticathode of Group B. Since the rays have to pass through the Al window they must contain a certain amount of the Al characteristic radiation. If the generating potential is low enough, the radiation will consist wholly of this Al characteristic. But with increasing generating potential the primary rays from the anticathode will become hard enough [stage (α)] to penetrate the window and so form a constituent of the emergent radiation. Further increase of the generating potential will have no influence on the quality of the secondary radiation from the window, but it will have the effect of increasing the penetrating power of the primary radiation from the anticathode. A stage will be reached when this primary radiation will possess a penetrating power greater than that from the window. A representative member of Group A can be regarded as emitting a radiation which is the same as that from a typical member of Group B with the addition of a strong secondary radiation from the anticathode itself. This strong secondary radiation can be regarded as the partial return in the direction of observation of the forward directed hemisphere of radiation spreading down into the anticathode. In the case of anticathodes of Group B it is supposed that this forward hemisphere is absorbed and lost in the anticathode, although of course it may be partially scattered.

Fig. 2 will now be readily understood. It is intended to represent in a quantitative sort of way possible analyses of the radiations from members of Groups A and B at two different cathode ray velocities corresponding to generating potentials V and V_1. The figure, for simplicity, takes Al as typical of Group A. PQ represents, in section, the plane of the window

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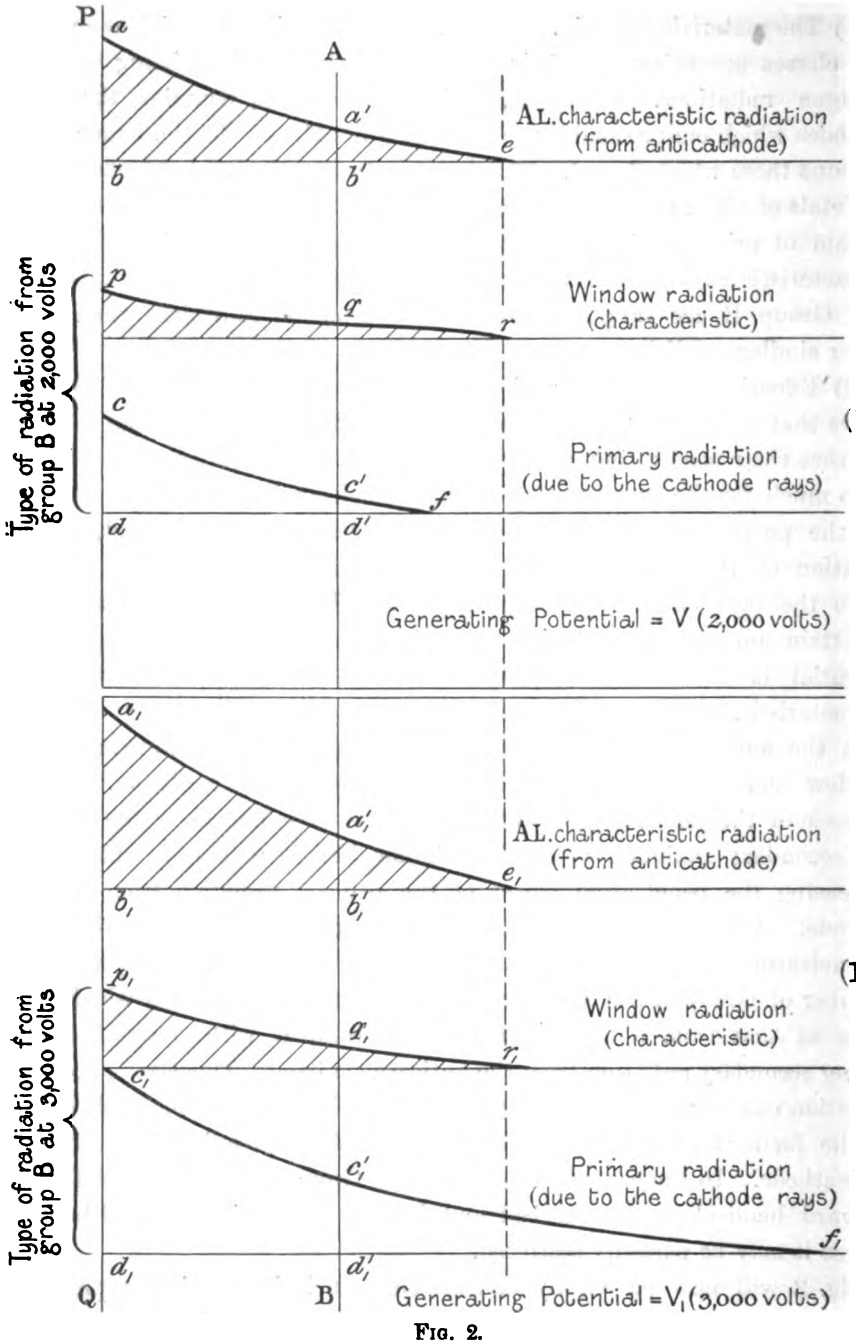

FIG. 2.

distances measured at right angles to PQ representing actual distances at right angles from the window. Take the top curve *aa'e*, which represents

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the characteristic radiation from an Al anticathode at V volts. The radiation represented by this curve can penetrate no further than the distance *be*, or, rather, beyond *e* it produces no measurable ionisation. Further, the area included between *aa'e* and *be* represents the energy of the emerging radiation as measured by the ionisation produced on its total absorption. If, however, only the radiation to the right of *a'b'* be absorbed, then the observed energy (ionisation) will be given by the area included between *a'e* and *b'e*.

These explanatory remarks apply equally to the other five curves. It may be here pointed out that of the six curves in fig. 2, four possess the same penetrating power, and, in fact, are representatives of the same type of radiation produced under different circumstances. These four curves are shaded in the diagram.

In fig. 2, $V < V_1$, indicating that the variable primary constitutent *cc'f* is less penetrating at V volts than the corresponding constituent $c_1c_1'f_1$ at V_1 volts. Consider (i) of fig. 2 first of all. The two bracketed curves *pqr* and *cc'f* represent the constitution of the radiation from some member of Group B. The invariable window radiation is represented by *pqr*, while the primary component (at this potential supposed to be softer) is represented by *cc'f*.

The total ionisation produced by this radiation

$$= [\text{area } pqr + \text{area } cc'f].$$

The total ionisation which would be produced by any other member of Group B would be

$$= s\,[\text{area } pqr + \text{area } cc'f],$$

where *s* is the appropriate constant.*

Now the constitution of the radiation from an Al anticathode can be represented by the three curves *aa'e*, *pqr*, and *cc'f*, the latter two curves requiring a suitable factor when their areas are taken into account. The curve *aa'e* represents the secondary characteristic radiation spreading out from the anticathode.

The total ionisation produced by this radiation

$$= \text{area } aa'e + \alpha\,[\text{area } pqr + \text{area } cc'f].$$

The area *aa'e* is here much the more important, since α is a factor much less than unity. This factor is introduced because, apart from the secondary radiation represented by the area *aa'e*, the Al radiation is the same as that from members of Group B, only on a smaller scale.

* This involves the assumption that a linear connection exists between the energy of the primary and that of the window radiation.

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Turning to (ii) of fig. 2, representing the constitution of the radiations at V_1 volts, we notice the main differences. The variable primary constituent $c_1c_1'f_1$ is here shown to be more intense and somewhat penetrating, while the aluminium characteristic radiation from the anticathode has considerably increased in ionising value.

We are now in a position to write down in terms of the areas of these curves expressions for the radiation values* of Al and of members of Group B. It is clear from the definition that in the case of a member of Group B, the relative radiation value is equal to s, the constant already introduced. It is shown below that the radiation value of a member of Group A cannot be so simply expressed, but depends on the method of measuring the ionisation.

Expressions are obtained for the radiation value of Al, firstly taking account of the areas of the complete curves to the right of PQ, and, secondly, only taking account of the areas to the right of AB. The first method involves the measurement of "total ionisation," while the second involves the measurement of what may be termed "end ionisation."

1. *Method of "Total Ionisation."*

The relative radiation value ${}_{V}R_{T}$ at V volts of the Al anticathode is given by

$$ {}_{V}R_{T} = \left(\frac{\text{area } ae + \alpha\,[\text{area } pr + \text{area } cf]}{\text{area } pr + \text{area } cf}\right) 100. $$

Not much error will be introduced by neglecting the effect of the window; in which case

$$ {}_{V}R_{T} = \left(\frac{\text{area } ae + \alpha \text{ area } cf}{\text{area } cf}\right) 100 = \left(\alpha + \frac{\text{area } ae}{\text{area } cf}\right) 100. $$

Similarly

$$ {}_{V_1}R_{T} = \left(\frac{\text{area } a_1e_1 + \alpha \text{ area } c_1f_1}{\text{area } c_1f_1}\right) 100 = \left(\alpha + \frac{\text{area } a_1e_1}{\text{area } c_1f_1}\right) 100. $$

* The relative radiation value of an anticathode A is given by the defining relation

$$ R_A = i_A/i_S \times 100, $$

where R_A = the relative radiation value of an anticathode A,

i_A = the energy of the Röntgen rays emitted by A,

i_S = the energy of the rays emitted under the same experimental conditions, by a standard anticathode S,

100 = the standard radiation value at all generating potentials of the standard anticathode.

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2. *Method of "End Ionisation."*

If ${}_{V}R_{E}$ and ${}_{V_1}R_{E}$ are the relative radiation values, using this method at V volts and V_1 volts respectively, then

$${}_{V}R_{E} = \left(\frac{\text{area } a'e + \alpha \text{ area } c'f}{\text{area } c'f}\right) 100 = \left(\alpha + \frac{\text{area } a'e}{\text{area } c'f}\right) 100,$$

$${}_{V_1}R_{E} = \left(\frac{\text{area } a_1'e_1 + \alpha \text{ area } c_1'f_1}{\text{area } c_1'f_1}\right) 100 = \left(\alpha + \frac{\text{area } a_1'e_1}{\text{area } c_1'f_1}\right) 100.$$

From the diagrams in fig. 2 we see at once from these expressions that

$${}_{V}R_{T} < {}_{V}R_{E}, \quad \text{and} \quad {}_{V_1}R_{T} > {}_{V_1}R_{E},$$

while between V and V_1 there must be some potential V_x where ${}_{V_x}R_{T} = {}_{V_x}R_{E}$.*

We see that, on the views suggested, the relative radiation value of an Al anticathode should depend entirely on the fraction of energy absorbed by the measuring apparatus. That this is experimentally the case is shown in Table I, where it is seen that the potentials corresponding to V and V_1 are 2000 and 3000 volts respectively.

The same theory applies to the case of a Pt anticathode, which emits a strong secondary radiation of much the same penetrating power as that from aluminium.

§ 3. The Dependence of the Energy of Röntgen Radiation—

(A) *On the Nature of the Anticathode.*

(B) *On the Velocity of the Parent Cathode Rays.*

It is well known that all metals do not make equally efficient anticathodes. Kaye,† for example, found that, using cathode rays of rather high velocity, they could be arranged in descending order of efficiency, uranium being at the head of the list and titanium at the foot.

His experiments were carried out in the following general way:—An ionisation chamber was subjected to the action of Röntgen radiation from various anticathodes and the ionisation currents measured. From the value of these ionisations the relative radiation values of the anticathodes (a standard anticathode having been chosen) were calculated from the defining relation already given

$$R_A = i_A/i_S \times 100,$$

where

R_A = the relative radiation value of an anticathode A,

i_A = the ionisation current produced by an anticathode A,

i_S = „ „ „ the standard,

100 = the value assigned to the radiation value of the standard.

* In this case f and f_1 would fall on the dotted line of fig. 2.

† G. W. C. Kaye, 'Phil. Trans.,' A, vol. 209, p. 137.

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A list drawn up in this way cannot be satisfactorily interpreted unless the absorption coefficients in air of the radiations are known. For an anticathode occupying a high place in the relative radiation scale may owe its position to the emission of very absorbable rays, which will, of course, produce great ionisation in the chamber—which in Kaye's experiments only partially absorbed the rays dealt with. In the present experiments the radiations are totally absorbed, and therefore the results are not open to objections of this nature.

The experimental results of the first part of this section show how the relative radiation values of a number of anticathodes depend on the velocity of the cathode rays incident on them. The experiments were carried out using cathode rays generated at steady potentials ranging from 1600 to 3600 volts, corresponding to velocities between $2{\cdot}4 \times 10^9$ and $3{\cdot}7 \times 10^9$ cm./sec.

The results are shown in fig. 3, and may be verbally stated as follows :—

1. The relative radiation values of the anticathodes Ag, Pb, Sn, Sb, Ni, Cu, Fe, Zn,* are independent of the velocity of the parent cathode rays.

2. The relative radiation values of Al and of Pt rise rapidly as the velocity of the parent cathode rays increases.

Before these relative radiation values can be regarded as quantitatively reliable it will be necessary to be quite certain that the finish of the anticathode surface has no effect. This is a matter requiring experimental investigation. It is quite conceivable that such a surface effect might exist (more especially with slow cathode rays), but even if its existence were proved it would not affect the validity of conclusions based on the *variation* of the radiation values with the generating potential.

The radiation values found under the experimental conditions of this investigation in no way agree with those found by Kaye (*loc. cit.*). These discrepancies are perhaps due to secondary emissions at the high potentials which he used. The graph shows very clearly how it is possible for Al—in spite of its low atomic weight and density—to be the most efficient anticathode between certain limits of cathode ray velocity.

These results were obtained using the particular ionisation chamber arrangement of fig. 4, in which the window of the discharge tube is connected to the case of the chamber and charged to a saturating potential. By this means the total ionisation (see § 2) was measured, since the chamber was long enough to totally absorb the radiation involved.

Now the ionising radiation has had to pass through 0·002 cm. of aluminium window—a thickness which at this stage of the experiments was as small as could be conveniently manipulated. It was thought that interesting results

* Hereafter (and in § 2) referred to as members of Group B.

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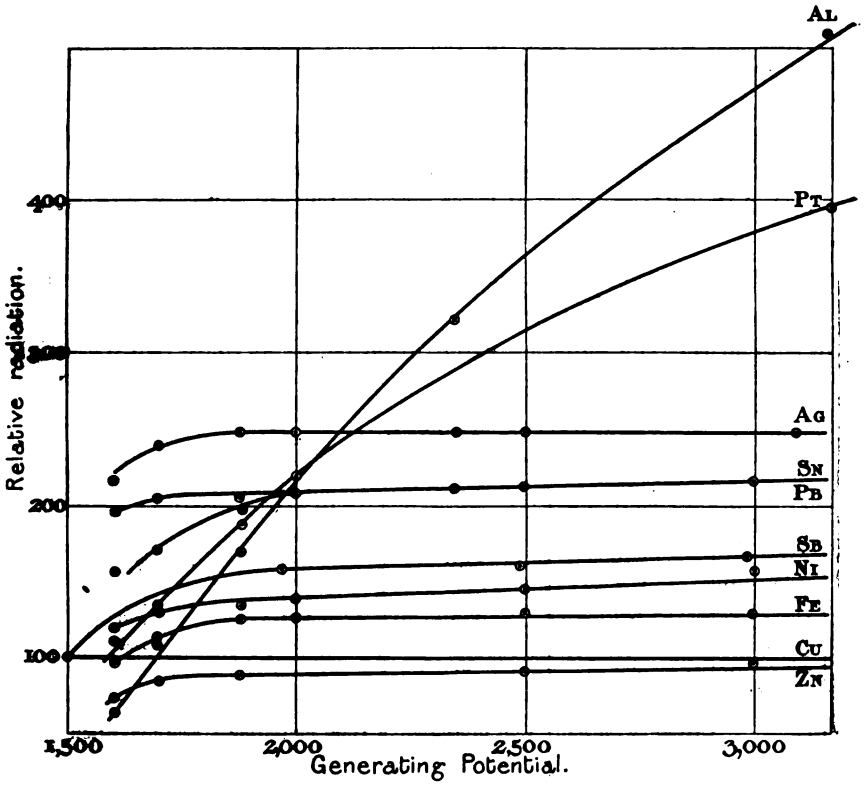

FIG. 3.

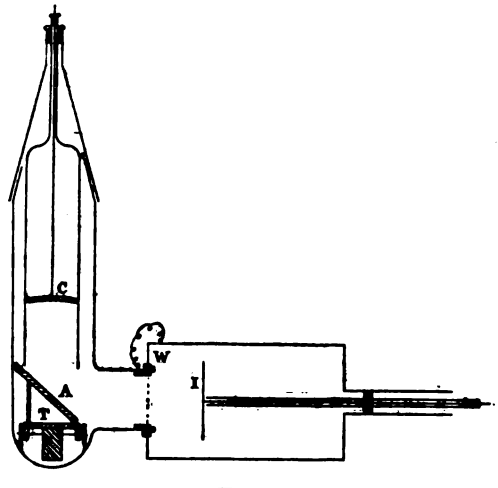

FIG. 4.

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might be obtained by repeating the experiments just described, using a thicker window or an effectively thicker one. In this way, it was thought, light might be thrown on the constitution of the different radiations. This end was attained experimentally by means of the arrangement of fig. 1, in which the gauze front N is a centimetre or so from the window W. The total ionisation is thus not measured, since the ionisation between W and N is not included. We may use the term "end ionisation" to denote what is measured.

The relative radiation values found in this way at generating potentials of 2000 and 3000 volts are given in the following table, which includes, for the sake of comparison, the radiation values from fig. 3* at these two potentials.

Table I.

Cu	100	100	100	100
Pt	**227**	**302**	**400**	**100**
Sn	229	243	236	240
Al	**226**	**298**	**515**	**220**
Ag	262	251	266	281
Fe	132	138	128	122
Cd	112	112	127	136
Ni	152	150	148	144
Zn	93	97		
	Total ionisation. Fig. 4.	End ionisation. Fig. 1.	Total ionisation. Fig. 4.	End ionisation. Fig. 1.
	2000 volt radiation.		3000 volt radiation.	

It will be observed that again Al and Pt, as representative members of Group A, are differentiated from members of Group B, but in this case by *the dependence of their relative radiation values on the amount of energy absorbed by the ionisation chamber.* These results follow from the theory given in § 2 and are easily remembered by its aid.

We have now seen how the *relative* intensity of Röntgen radiation from some anticathodes varies with the velocity of the parent cathode stream. It yet remains to see how this velocity determines the actual energy radiated.

The results for a nickel anticathode are shown in fig. 5, the arrangement of fig. 4 being used. This experiment is but barely alluded to, as I am making it the basis of a separate research. From the graph it will be seen that very little radiation emerges from the window below 1200 volts, at which potential a quite sudden coming-in of ionisation is followed by a linear

* Making use of "total ionisation," by use of fig. 4.

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connection between energy of radiation and generating potential (the current passing through the tube being kept constant).

The generating potential, 1200 volts, at which the issuing radiation begins to become appreciable does not depend to any large extent on the thickness

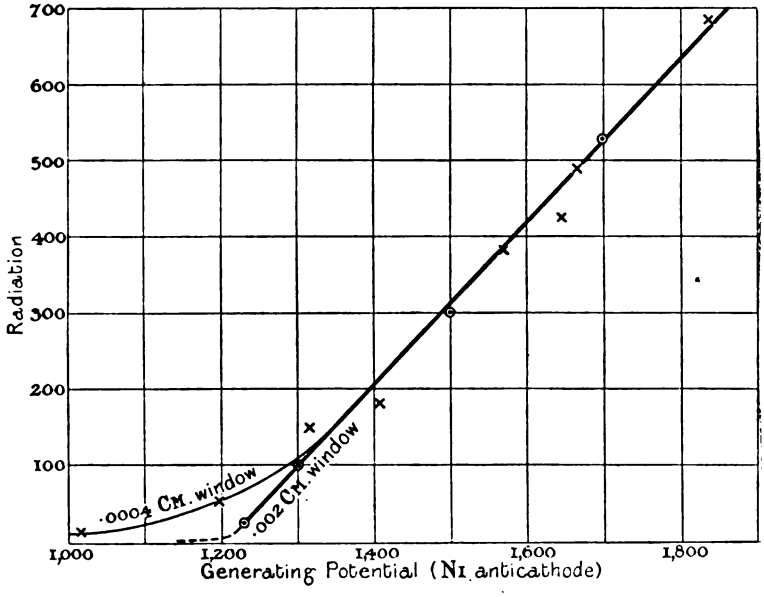

FIG. 5.

of the window. This is shown by the points ⊙ and × on the graph obtained with two different thicknesses of window 0·002 and 0·0004 cm. Preliminary experiments have indicated that the curve of fig. 5, so far as shape is concerned, is the same for all anticathodes as for Ni.

The generating potential 1200 volts, corresponding to a cathode ray velocity of $2{\cdot}1 \times 10^9$ cm./sec., will, on the view put forward in this paper, furnish a value for the minimum cathode ray energy capable of stimulating the Al characteristic radiation.

§ 4. The Dependence of the Absorption Coefficients of the Röntgen Radiation on—

(A) *The Nature of the Anticathode.*

(B) *The Velocity of the Parent Cathode Rays.*

Absorption curves in Cu of the 3000 volt radiation from all the anticathodes are plotted in fig. 6, where the logarithm of the radiation intensity is plotted along the y axis and the thickness of the screen in arbitrary units along the x axis. The ionisation produced after absorption of the

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rays in a thickness of copper equal to 5 in fig. 6 is put equal to 100 units. The arrangement of fig. 1 was used, the distance between W and N being about 1 cm., so as to admit the slide carrying the absorbing screens.

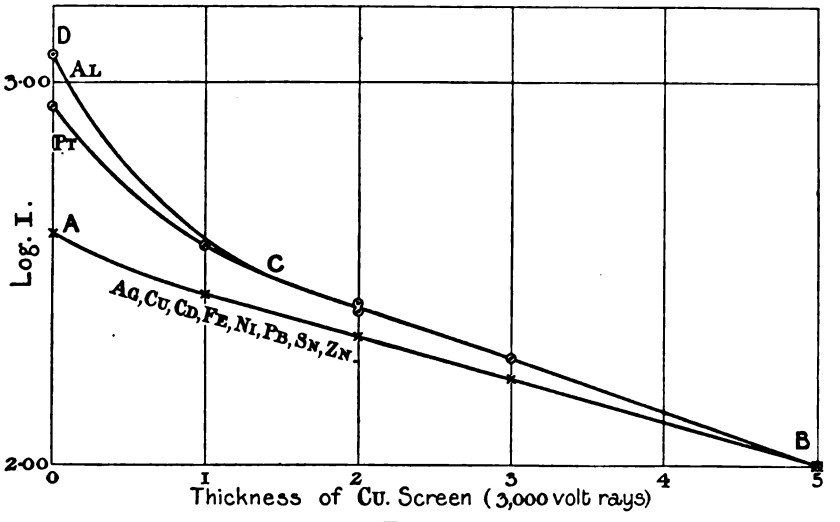

Fig. 6.

It follows from the graph that once again Al and Pt stand apart from the remaining anticathodes. In this experiment their absorption curves have an early steep part, whereas the similar curves for members of Group B are coincident straight lines with just a very slight initial steepening.

These experimental results can receive only one interpretation, and that is that the 3000 volt radiation from members of the B group of anticathodes is very nearly homogeneous and independent of the nature of the anticathode,* whereas that from Al and Pt contains not only a radiation of the same penetrating power as that from Group B, but also one of a considerably softer character.

I have plotted absorption curves similar to those of fig. 6 at different generating potentials, and it seems that (using an Al anticathode) the part CB of the absorption curve DCB becomes steeper as the generating potential diminishes. At 2600 volts, or thereabouts, CB disappears, and the complex curve DCB degenerates to practically a straight line,† corresponding to the earlier steep part DC. At potentials less than 2600 volts the slope of DC remains much the same, although the intensity of the radiation itself is

* J. J. Thomson, "On the Electrical Origin of the Radiation from Hot Bodies," 'Phil. Mag.,' Aug., 1907, p. 230. This paper anticipates theoretically this experimental result.

† The radiation is not quite homogeneous.

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continually diminishing. When an anticathode of Group B is used instead of Al, much the same sequence occurs, only in this case the energy escaping from the tube is much less.

The variation in absorption coefficient λ/ρ with the generating potentials in volts is shown in fig. 7.

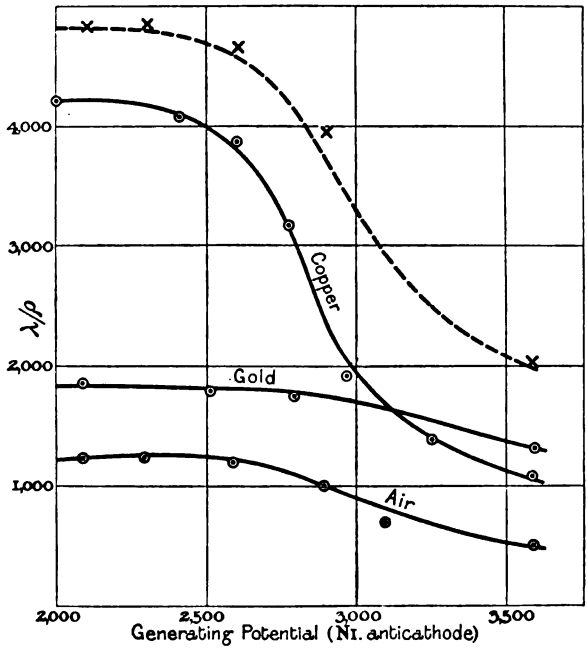

FIG. 7.

In these experiments a Ni anticathode, as representative of Group B, was used. The absorption coefficients plotted in fig. 7 correspond to the early part of the curves of fig. 6, taken of course at different potentials. The graphs show how the slight initial steepening observable at 3000 volts becomes very important at lower generating potentials, when, on the theory of § 2, the variable primary constituent of the examined radiation is becoming of less importance. These absorption coefficient variations have been observed for screens of gold, copper, tin, air,* and aluminium. With the exception of the latter the general results are independent of the material of the screen.

From fig. 7 it is clear that, taking the air curve as typical, the absorption coefficient of the radiation issuing from the tube is up to 2600 volts independent of the generating potential.† At generating potentials above

* The dotted curve of fig. 7 is the air curve with its ordinates quadrupled.

† This remarkable result has already been obtained with Al screens for a similar range of generating potentials by W. Seitz, 'Phys. Zeitschr.,' 6 Jahr., No. 23, p. 757.

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2600 volts the graph shows a sudden diminution in λ/ρ, and the value of V at which this drop takes place is independent of the screen. The potential at which this diminution in λ/ρ appears must depend on the thickness of window used, because drawing the ionisation chamber further away from the window has the effect of shifting the bend in the curve towards a higher value of V.

It will be clear that up to 2600 volts or thereabouts the radiation emerging from the window or, rather, entering an ionisation chamber a centimetre away, is mainly (to within a few per cent.) the aluminium characteristic radiation. The absorption coefficients of this radiation (using the 2700 volt radiation from Al) in various absorbing screens are shown in the following table. The very high values for Cu and Ag screens are noteworthy.

The last column shows the parallel coefficients for the softest characteristic radiation studied by Barkla, namely, that from chromium :—

Table II.

Screen.	λ/ρ.	λ/ρ (Cr radiation).*
Pt	2010	516·8
Au	1760	507
Cu	3900	143
Ag	2020	580·5
Sn	1030	713·7
Al	580	136
Air	1150	—

* Barkla and Sadler, 'Phil. Mag.,' 1909, vol. 17, p. 749.

It has been mentioned that the curves of fig. 7 are of the same general shape for the screens Au, Cu, Sn, and air, but this does not quite hold in the case of Al screens. The horizontal part of the curve persists for a rather greater distance, and shows in fact a very slight tendency to rise before finally falling towards the V axis.

§ 5. The Corpuscular Radiation excited by the Impact of Soft Röntgen Rays on Metallic Surfaces.

For the purposes of the experiments described in this section the ionisation chamber was cemented on to the discharge tube in the manner shown in fig. 4. By means of liquid air and a charcoal tube the chamber could be evacuated.

The Röntgen rays from the aluminium anticathode passed through the window W and fell on the plate I. When the plate I was Cu, Pb, Ni, Ag,

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or Zn the same effects were always observed, viz., that that plate received a negative charge. This was proved to be due to the emission of negative particles from the window by applying a strong magnetic field across it. When the magnet was "on" no deflection could be observed in the electroscope in two minutes. When the magnet was "off" the rate of negative charging up of the electroscope was about two divisions a minute, the current through the discharge tube being 1/5 milliampère at 3400 volts.

When the plate A was either aluminium or platinum, the incidence of the rays caused the electroscope to charge up positively, the rate being increased considerably when the magnetic field was switched on. The conclusion is, therefore, that the emission by aluminium and platinum of a strong secondary Röntgen radiation is accompanied by an emission of corpuscles.

§ 6. Summary and Conclusions.

1. The variations with the generating potential (which is proportional to the (velocity)^2 of the primary cathode rays) of the relative radiation values of 10 anticathodes have been studied. The potential limits were 1500 to 3600 volts. Eight of these anticathodes (members of Group B) were found to have definite radiation values not depending on the generating potential, while the remaining two (Al and Pt) rapidly increased their radiation values with rising potentials.

At any definite generating potential the actual radiation values of Al and Pt depend enormously on the amount of energy absorbed by the ionisation chamber, whereas the radiation values attached to the members of Group B are not so influenced.

If a particular view of the constitutions of the radiations be taken (see § 2) these results are easily explained, and, moreover, fall into line with other results of an entirely different kind. Briefly this view is as follows:—

The behaviour of the 10 anticathodes studied under the particular experimental conditions of this research leads to their classification under two headings, termed for convenience Groups A and B. At a definite generating potential the radiations from members of Group B are regarded as differing amongst themselves only in quantity (ionising power) (fig. 3) and not in quality (absorption coefficient) (fig. 6). The quality, however, does depend on the generating potential (fig. 7).

The radiations from anticathodes of Group A (Al and Pt) also are regarded as containing a component whose quality depends on the generating potential. But they are also imagined to contain relatively strong constituents of the characteristic type, which are peculiar in their possible possession of absorption coefficients less than those of the exciting primary rays. In other words

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it is supposed that these characteristic radiations can be stimulated by less penetrating exciting rays.

Such an hypothesis is not glaringly absurd, since the law to which it does not conform is after all only a restatement of Stokes's law of light fluorescence, and Prof. R. W. Wood has shown its limited applicability.

2. Below a generating potential of 1200 volts only a very weak Röntgen radiation can be detected. This is regarded as a secondary effect of the window. The sudden coming in of relatively strong radiation at 1200 volts is very striking (fig. 5). Above 1200 volts there is a linear connection between the energy of the Röntgen rays emerging from the tube and the energy absorbed by the discharge, the current through the tube being kept constant.

3. Over a certain range of generating potentials the speeding-up of the parent cathode rays produces no effect on the absorbability of the emerging radiation (fig. 7). This also is regarded as an effect due to secondary radiation from the window.

In fact with the measuring chamber 1 cm. from the Al window the view held is that the only radiation which is measured below 2600 volts is, with any anticathode, the aluminium characteristic radiation.

At 3000 volts the radiations from Al and Pt and members of Group B have been analysed, and the results show conclusively the emission of secondary radiation from the former two, and its almost complete absence in the rays emitted by the latter eight.

4. It has been shown that Al and Pt under the impact of these soft rays emit corpuscular radiation in addition to the above-mentioned secondary Röntgen radiation. In this respect again Al and Pt are differentiated from members of Group B, which do not emit under similar circumstances any measurable quantity of charged particles.

It gives me pleasure to thank Prof. Sir J. J. Thomson for his interest in this investigation, which was carried out at the Cavendish Laboratory.

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Experiments on Stream-line Motion in Curved Pipes.

By JOHN EUSTICE, B.Sc., Professor of Engineering, Hartley University College, Southampton.

(Communicated by Sir Joseph Larmor, Sec. R.S. Received January 26,—Read February 16, 1911.)

Author's previous Experiments.—In the paper read by the author on the "Flow of Water in Curved Pipes," before the Royal Society on June 2, 1910, it was shown that even a small curvature in the length of a cylindrical pipe affected the quantity of flow of water through the pipe. The effect at velocities below the critical velocity for a straight pipe was most remarkable, inasmuch as the experiments showed that in coiled pipes there was apparently no critical velocity region, whilst in less pronounced curves, where the critical velocity is not entirely absent, a very slight sinuosity of the pipe lessened the flow. This was shown by the increase in the value of the index n in the formula, $s = Kv^n/m$ from $n = 1$, for perfectly straight pipes, to $n = 1{\cdot}1$ to $1{\cdot}2$ for pipes slightly curved or sinuous. Here s or h/l is the hydraulic gradient, v is the velocity of flow, m is the hydraulic mean radius, and K is a constant.

In an attempt to discover the cause of this departure from the law of flow in straight pipes, the author had tried Prof. Osborne Reynolds' colour-band test in a coiled glass tube, but the arrangements were of a primitive character and the results obtained were not decisive. At the suggestion of Sir Joseph Larmor the colour tests have been repeated with specially made glass tubes, in which the stream motion could be traced by the introduction of coloured water through capillary nozzles.

Arrangements for Coloured Filaments.—The following arrangement was adopted:—A brass tube A (fig. 1) of about 2 cm. internal diameter was fitted internally with a piece of brass B of boat-shaped section, into which six separate supplies of dyed water could be introduced through the nipples shown in fig. 1. The dye was supplied from the open tubes T, the height of each of which could be adjusted so as to allow the dye to flow in a gentle stream from the nozzles N, N, which were 1·25 mm. external and 0·3 mm. internal diameter.

The supply of water came from a tank through a cock at C; to this was connected the pipe which contained the nozzles. The water from the tank in its passage past the nozzles carried the dyes with it. The direction of flow is shown by the arrows, the velocity of flow was regulated by a pinch-cock PC placed on a flexible tube at the outlet end of the tube under

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observation. Glass tubes of various shapes could be connected at the joints J, J, and the stream-line motion made visible by the dyes could be observed and photographed or sketched.

In order to trace the paths of the streams of dye from each nozzle separately, six different colours were used, the nozzles and supplies of colour being so arranged that the stream from each could be observed separately; by an adjustment of the tube which contained the nozzles, every part of the tube could be investigated.

In fig. 1, six streams of dye are shown passing through the conical glass

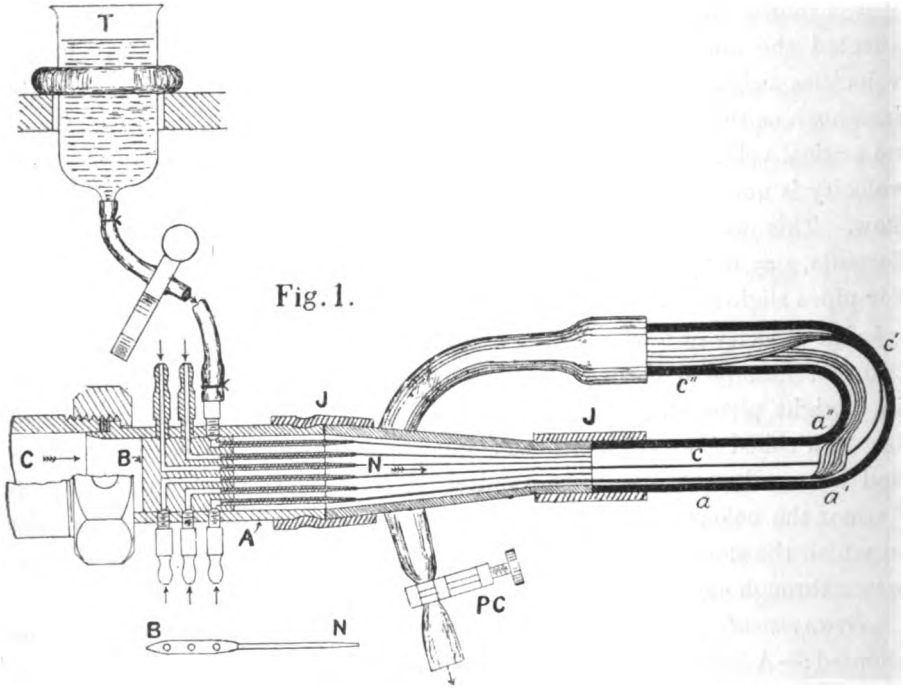

Fig. 1.

connecting tube JJ; the paths of two only of the filaments are traced in the U-tube. In fig. 2 the complete paths of six such colour bands are traced.

The first tubes experimented on were U-shaped, as shown in figs. 1 and 2; the experiments in these tubes are described in detail, since they illustrate the methods adopted for other curved tubes.

For the purpose of observing and photographing the stream-lines, the U-tube, with its central plane horizontal, was placed in a tank; mirrors with their planes at an angle of 45° with the plane of the U-tube were arranged in positions for obtaining the side and end elevations. In order to lessen the effect of refraction, the tube was completely covered with water; photo

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graphs were taken of the tube and the reflections, and sketches were made from which fig. 2 has been drawn.

The photographs and drawing show the character of the stream-lines, but it is impossible to reproduce the extremely beautiful effects due to the interlacing of the colour bands. Although each band kept distinct from the others it was necessary when tracing out the stream-lines to shut off all the colour bands except the one under observation.

Results obtained in U-*tubes.*—A stream filament *a* (figs. 1 and 2) if it is in the central plane of the tube and close to the outer wall of the bend, breaks up into two parts immediately it reaches the curve of the bend, each of which leaving the central plane in opposite directions and following the wall of the tube crosses to the inner wall, and coming towards the central plane the divided filament forms the loop shown in the end elevation of the bend (fig. 2); the filament is now spread out into a narrow band and passes through the outlet limb, the path taken being shown by the lines *a*, *a*.

Stream filaments which are near the outer wall of the tube and just above (or below) the central plane will cross the bend as shown by the line *b* (fig. 2), and follow the surface of the tube, keeping above (or below) the central plane.

The behaviour of other filaments which are not in the central plane of the tube may be seen from the paths of *c* and *d*. Both these lines strike the outer wall of the bend and cross over near the surface of the tube, *c* to the inner wall of the bend and *d* to the inner wall of the outlet limb. The filaments *e* and *f* pass around the bend and do not strike the walls.

Several U-shaped tubes, right angled bends, and other tubes bent in curves of large radius were experimented on; some of these are illustrated in the diagram (figs. 3 to 7). The tubes are drawn accurately to scale. The radius in centimetres of the centre line of the curve is in each case given by the number printed at one end of each tube. The drawings of the stream-lines in fig. 2 are from sketches and photographs of some of the experiments.

In fig. 3 (2) the filament *a* strikes the outer wall at A (which is near the central plane of the tube bend), where it spreads out into a flat band and after following the wall of the tube it strikes the inner wall at A′ and then takes the form of path shown; a section of such a colour band after leaving A′ is usually curved.

In fig. 3 (4) the colour bands *b*BB′ and *c*CC′ illustrate the effect of increasing the velocity, *c*CC′ being at a mean velocity of flow of 3·7 cm. per sec., whilst *b*BB′ is at a velocity of 11 cm. per sec. In fig. 3 (6) the band *d*DD′ after leaving D′ breaks into branches, the main portion D′*d*′ flowing near the centre of the outlet limb whilst D′*d*″ flows near the inner wall of the tube.

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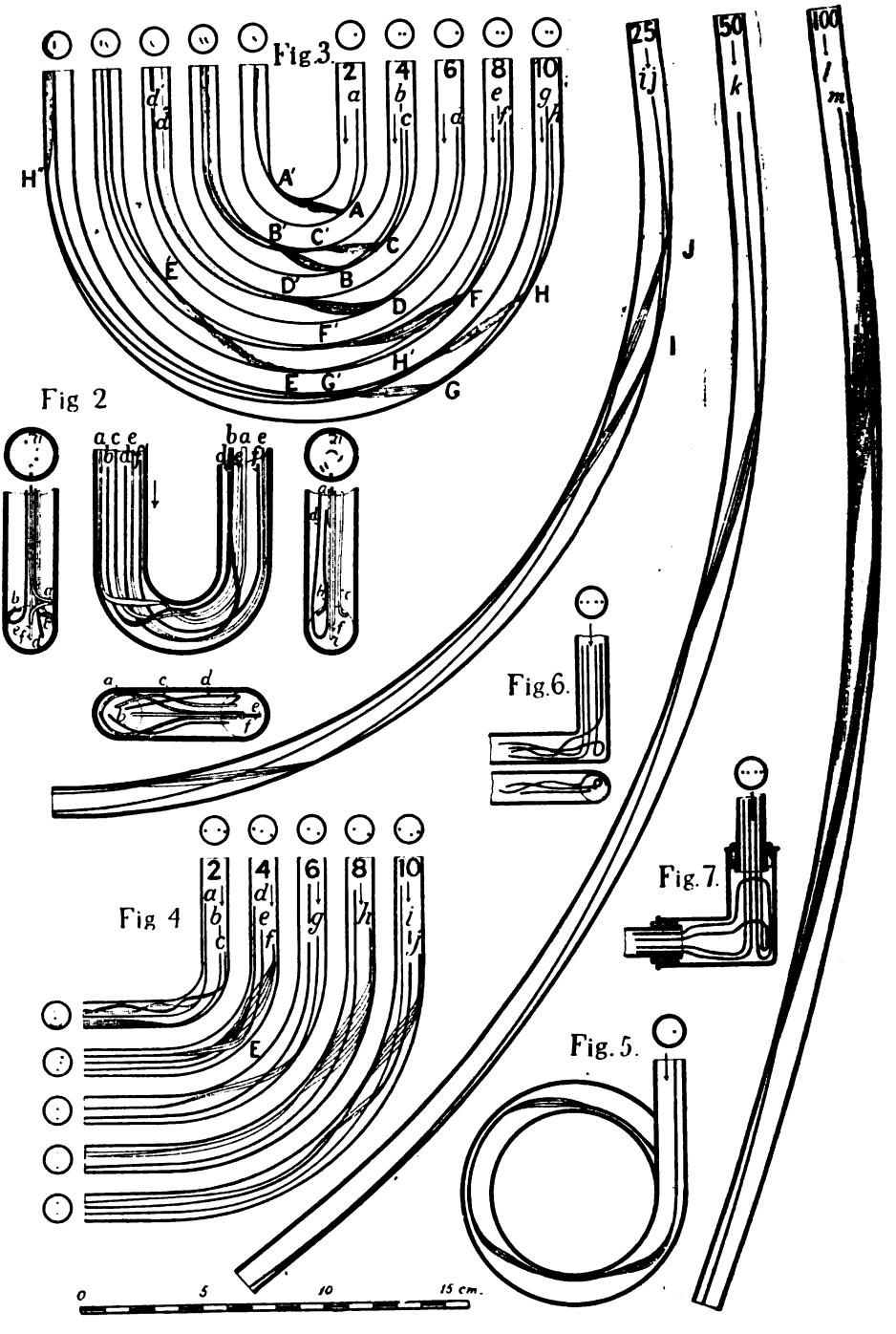

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In fig. 3 (8) the line *f*FF′, taken at a velocity of 4·6 cm. per second, is of the same character as the lines previously described; after striking at F, it spreads out into a wide band, collects at F′ and leaves the tube in a fairly regular band of colour. The line *e*EE′ shows the effect of increasing the velocity to 18 cm. per second.

In fig. 3 (10) the line *g*GG′ is at a velocity of 17·5 cm. per second and the line *h*HH′ is at a velocity of 5·5 cm. per second, just sufficient for the colour band to strike the outer wall of the curve at H″, the band then spreads as shown in the sketch.

The effect of increasing the velocity in a curved tube is to increase the curvature of the filaments; for example the band H′H″ which is shown touching the tube at H″ would pass down the outer straight part of the tube without touching it if the velocity of flow is increased; other examples of this are given in the right-angled bend fig. 4 (2) and in fig. 1, *cc′c″*.

Results in Tubes of large Radius.—The same general results are obtained in tubes in which the radius of curvature of the tube length is large; fig. 3 (25) illustrates the effect of doubling the velocity of flow in a tube 1 cm. diameter bent to a curve of 25 cm. radius; the line *j*J (velocity 5·5 cm. per second) shows the repeated crossing of the colour band; *i*I is at double the velocity of flow (11 cm. per second). The increased curvature of the band at the higher velocity is again apparent.

The filament *k* in fig. 3 (50) and *l* in fig. 3 (100) show that, even when the curvature is very small, if the curve is sufficiently long the stream-lines will all strike the outer wall and follow the surface of the tube to the inner wall. The filament *m* in fig. 3 (100) enters the straight part of the tube in the central plane close to the outer wall; it spreads out into wide bands both above and below the central plane, and after crossing the tube opens out into two bands which remain uncombined for the whole remaining length of the tube, the inner radius of the bend being quite free from colour. In a longer tube these bands would cross over again to the outer radius, as is shown in the coiled tube, fig. 5, where all the stream-lines repeatedly cross from the inner wall to the outer wall and back.

In a straight tube the colour bands remain distinct and the surrounding water is not tinted; in curved tubes after the colour bands strike the walls of the tube, although the bands can be distinctly traced, some of the colouring matter is dispersed into the surrounding water, the outlet water being tinted.

In a coiled tube of several convolutions the distinctive character of the colour filament is gradually lost and after passing through several coils can scarcely be traced.

Results in right-angled Bends.—In the series of right-angled bends illustrated

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in fig. 4, the lines *a*, *b*, *c*, in (2) were taken at a velocity of 10·5 cm. per second; when the velocity was increased to 15·2 cm. per second the positions of all the lines changed slightly, the line *a*, which at the lower velocity was in the position of the regular curve shown, broke up at the higher velocity into two branches, one of which formed a spiral vortex near the central plane of the tube and interlaced with the line *c*.

The position of the filament *b* was arranged so that it struck the extreme part of the outer curve, where it scattered as shown; at the increased velocity the line *b* passed through the outer straight tube without scattering.

In (4) the velocity is 7·3 cm. per sec., the line *f* strikes the bend below the central plane and crosses over close to the surface of the tube; other lines, such as *e*, which are above the central plane, follow paths shown at *e*E, whilst the lines represented by *d* nearer the central plane and the inner surface of the tube pass around the bend in an unbroken curve.

In (6) the velocity is 12·5 cm. per sec., the line *g* crosses under the other line, which passes through in an unbroken curve.

In (8) the velocity is 8 cm. per sec., the line *h* is close to the side of the tube near the central plane, it spreads immediately on entering the curved part, crosses the tube, and collects inside the bend, then leaves the bend in separate filaments; the other stream-line passes freely through the tube.

In (10) the velocity is 10 cm. per sec.; the results are very similar to that shown in (4).

The results obtained in sharp right-angled elbows are shown in figs. 6 and 7. The curious looping of the lines in fig. 7 will be understood from the somewhat similar loop shown in fig. 6.

The table on p. 125 is given to indicate the range of velocities employed, but the experiments were of a qualitative rather than of a quantitative character.

The U-tube, fig. 2, is 1·7 cm. internal diameter, all the others are 1 cm. diameter. The lengths of the curved part and the total lengths of each tube are given in Column 2. In each case the straight parts of the tube at both ends are of equal length.

Except in fig. 2 a connecting tube, 20 cm. long, was used in the position JJ, fig. 1; this tube tapered from 2 cm. to 1 cm. diameter for 10 cm. of its length, and was 1 cm. diameter for the remaining 10 cm. For fig. 2 the connector was only 4 cm. long, and tapered from 2 cm. to 1·75 cm. diameter.

The head in the tank varied from 20 to 30 cm.

Precautions taken in the Experiments: (*a*) To ensure the equal velocities of flow of the colour filaments and the surrounding water.—Before using

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1. Fig.	2. Length of tube, cm.		3. Radius of curve, cm.	4. Temp. °C.	5. Mean velocity of flow in diagram, cm. per sec.	6. Turbulent motion, cm. per sec.	7. Critical velocity by Reynolds' formula.
	Curved part.	Total length.					
Fig. 2	7·8	34·8	2·5	17·0	3·5	7—8	12·8
Fig. 3 (2) ...	6·3	50·0	2·0	18·0	*a* 10·0	17—27	21·5
Fig. 3 (4) ...	12·6	50·0	4·0	18·0	*b* 3·7, *c* 11·0	17—21	21·5
Fig. 3 (6) ...	18·8	50·0	6·0	18·5	*d* 7·8	18—20	21·3
Fig. 3 (8) ...	24·1	50·0	8·0	18·0	*e* 18·0, *f* 4·6	18—23	21·5
Fig. 3 (10) ...	31·4	50·0	10·0	18·0	*g* 17·5, *h* 5·5	20—26	21·5
Fig. 3 (25) ...	50·0	60·0	25·0	19·0	*i* 11·0, *j* 5·5	19—21	21·0
Fig. 3 (50) ...	50·0	60·0	50·0	18·0	*k* 10·0	20—21	21·5
Fig. 3 (100)...	50·0	60·0	100·0	18·0	*l* 12·6, *m* 6·4	20—21	21·5
Straight tube	—	60·0	∞	16·0	—	19—21	22·5
Fig. 4 (2) ...	3·1	13·1	2·0	19·0	10·5—15·2	18—20	22·5
Fig. 4 (4) ...	6·3	16·3	4·0	19·0	7·3	19—21	22·5
Fig. 4 (6) ...	9·4	19·4	6·0	19·0	12·5	18—20	22·5
Fig. 4 (8) ...	12·6	22·6	8·0	19·0	8·0	19—21	22·5
Fig. 4 (10) ...	15·7	25·7	10·0	19·0	10·0	19—21	22·5

the arrangement of nozzles and colour supply sketched in fig. 1, the author designed an apparatus for a single filament of colour which acted automatically so as to give equal pressures on the colouring liquid and the flowing water; it could be so arranged that at any pressure the coloured liquid would ooze very gently into the flowing stream.

In other tests the colour was allowed to accumulate in the tube BC, fig. 1, when no water was flowing; the colour was then shut off and water allowed to flow through the tube, the paths of the stream-lines could be distinctly traced, following the same general directions as in the case of the regular filaments.

The motion of the solid particles referred to on p. 129 is an additional proof of the effect produced not being due to the filaments having a higher velocity than the surrounding water.

The arrangement described above for single filaments was used for high pressure experiments in metal pipes, which were 150 cm. long and 1 cm. diameter. Between these pipes and the colour distributing nozzles was interposed a converging tube which was connected to the metal pipe by a glass tube, 15 cm. long, of the same diameter as the metal pipe; a similar glass tube was connected to the outlet end of the metal pipe. When the metal pipe was kept straight the colour filament showed distinctly in the

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glass tube at the outlet end; when the metal pipe was bent into a slightly curved form the colour filament no longer appeared in the glass tube at the outlet end as a thread of colour, but, if visible, it was as a flat band of colour, or it was more or less dispersed into the surrounding water.

Long, straight, glass tubes of from 1 to 2 metres long were substituted for the metal pipe, and when curved tubes were connected at the outlet end the same effect was produced as when the intervening connection was only a few centimetres long.

(*b*) Establishment of a steady *régime*.—From the preceding section (*a*) it will be seen that in some of the experiments the tubes were sufficiently long to ensure that the filaments and water had settled down to a steady *régime*.

In all the experiments the brass tube A, fig. 1, containing the nozzles for colour filaments was close to the tank, but between A and the tube experimented on there was interposed a converging tube, the dimensions of which are given on p. 124. This tube was of sufficient length to establish steady flow, as will be seen by comparing Columns 6 and 7 of the table.

Column (6) gives the commencement of the turbulent flow, Column (7) the critical velocity as calculated by Reynolds' formula. The same general results were obtained at low velocities when a steady *régime* is produced in a fairly short pipe at velocities far below the critical. In the U-tube, fig. 2, the connecting tube was short, and unsteady motion commenced at a much lower velocity than is given by Reynolds' formula. The turbulent motion given in Column (6) and the calculations in Column (7) are for the straight part of the pipe.

Comparison between the Flow of Water in Bends of Open Channels and of Closed Pipes.—Prof. James Thomson,* in his theory of the transfer of solid particles along the bed of a river from the outer to the inner bank, has shown that the centrifugal force of the more rapidly moving water near the surface overcomes that of the water close to the bottom, which is retarded by the friction of the bed of the river. Prof. O. Reynolds† has adopted this theory in his work "On Certain Laws relating to Rivers and Estuaries."

Thomson's experiments were carried out in open channels, and he has suggested that the theory of flow in curved channels is applicable to pipe bends. In introducing the theory he states that "a stream flowing along a straight channel, and thence into a curve, must flow with a diminished velocity along the outer bank and an increased velocity along the inner bank." The author's experiments show that the motion at the commence-

* 'Roy. Soc. Proc.,' May 4, 1876, vol. 25, and June 21, 1877, vol. 26.

† 'Report Brit. Assoc.,' 1887, and 'Sci. Papers,' vol. 2, p. 329.

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ment of the curve of a pipe bend is not that of a "free" vortex, for the velocity is greater near the outside than it is near the inside of a curve.

There is another difference between the two cases. In an open channel there is freedom in a vertical direction, and, as Thomson has pointed out, the difference of pressure between the inner and the outer banks causes the surface of the water to be inclined from the inner to the outer bank of the curve. No such freedom is possible in a pipe which is running full, hence it is probable that the curvature of the stream-lines is greater and the effect of pressure on the transfer of water from the outer to the inner curve is more pronounced in a pipe than in a channel.

In experiments on U-shaped open channels of semicircular section, about 1 cm. radius, the author has noticed that the flow of water near the surface is retarded, for if a filament enters the bend just below the surface MN in the position of 2, fig. 9, it divides so that a part goes under the stream, as in fig. 9; another part of the filament follows a somewhat similar course near the surface of the water and flows towards the centre of the stream, where it is carried around near the central curve of the bend. Filaments entering close to 1 behave in the same way, except that some of the colour is in this case carried slowly around the bend quite close to the outer radius.

With these differences between open channels and pipes the following explanation may be looked upon as an experimental confirmation of Prof. J. Thomson's theory when applied to curved pipes.

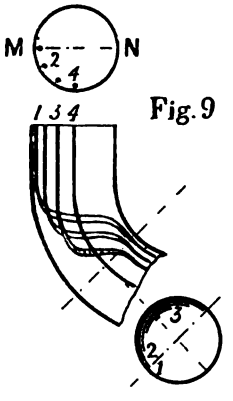

Fig. 9

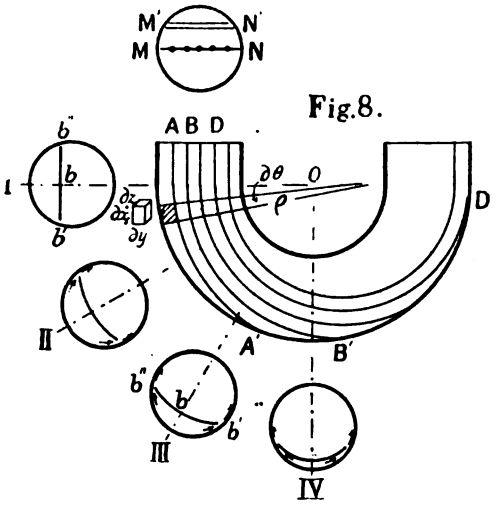

Fig. 8.

Motion in a Plane Sheet Perpendicular to Central Plane of Bend.—Consider a set of stream-lines flowing through the straight part of a pipe in a plane sheet which is at right angles to the central plane of the U-tube as shown

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at B and at $b''bb'$ (fig. 8) where the circles at I, II, III, and IV represent sections of the tube taken along the radial lines OI, OII, OIII, and OIV respectively. Since the stream-lines near the centre b of the sheet are flowing at a higher velocity than those nearer b' and b'', it follows that when the sheet enters the bend, the force required to make the stream-lines in the centre of the sheet (at b in section I) tend to follow the curve of the bend will be greater than the force required nearer b' and b'', that is to say, the pressure between b and the outer wall of the bend will be greater than the pressure nearer b' and b'', and a flow of water will take place along the path of least resistance, *i.e.* from the region of greater to the region of less pressure, in the directions shown by the arrows in II, III, and IV. The centre portion of the sheet will gradually approach the outer wall, whilst some portion of the water near b' and b'' will be carried round the inner wall of the tube.

Motion in a Sheet in the Central Plane of the Bend.—Consider the stream-lines flowing in the central plane MN of the tube (fig. 8). Changes in pressure above and below the central plane will have no effect in disturbing the position of the lines, since the tube is symmetrical on both sides of the plane MN. In any other sheet M′N′ which was parallel to the central plane before it entered the curved part, since there are less stream-lines, and the velocities are less than in the plane MN, the pressure at M′ will be less than the pressure at M, and the pressure at N′ will be greater than the pressure at N; hence there will be a flow of water from M to M′, that is to say, the water close to the surface of the tube, which in a straight tube is at rest, will even in a slightly bent tube be set in motion. As the flow of water from between a stream-line and the tube wall takes place, the stream-line will gradually approach the outer wall of the bend, the displaced water flowing around the walls of the tube from the outer to the inner wall of the bend. After entering the bend the sheet M′N′ becomes inclined in the direction of a normal to the curves $b''bb'$ (fig. 8), as is shown by the deviation of the filaments from the central plane in the left-hand view of fig. 2.

Motion of the Filaments near the Walls of the Tube.—The order in which the stream-lines flow around the walls is shown in fig. 9. A filament which approaches the curve at the outer radius of the bend strikes the tube and divides into two parts, each of which crosses a half circumference of the tube to the inside, as shown at 1. A filament at 2 which approaches farther from the central plane MN flows inside the filament 1. A filament 3 flows inside 2, and so on; this is represented in the lower section of the tube in fig. 9.

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It was often noticed that the colour filaments in the position of 2 and 3 crossed the tube in small waves or ripples, showing the approach of unstable motion, which ultimately leads to the mixing of the colour filaments with the surrounding water.

After reaching the inside of the tube the re-crossing always occurred in the half of the tube in which the filament entered, or in a tube of regular bore, the stream-lines are reflected back so as not to cross the central plane MN. This reflection is shown in some of the diagrams as in fig. 3 (10) and (25), and in the coiled tube fig. 5.

Turbulent Motion.—The experiments described above were carried out at velocities sufficiently low to give unbroken motion, but in all cases the effect of increasing the velocity was observed, and, although it was naturally impossible to trace the colour filaments for turbulent motion in the same way as has been done for steady motion, by increasing the quantity of dye or by placing finely divided solid matter in the tubes and carefully increasing the velocity until turbulent motion was reached, it was observed that the same general features hold good for turbulent motion. For example a layer of sand placed along the inside of the tube at aa' in fig. 1, in which the central plane of the tube is vertical, will not go around the outer radius of the U-tube but will follow the path $a'a''$. The author has shown that, when water is flowing at high velocity in a metal pipe bend, if a tube communicates from a' to a'' outside the tube a continuous stream of water is carried through the external tube from a' to a''.

Summary and Deductions.—The experiments show that when water is flowing at low velocities in a straight tube of uniform bore, filaments of colour maintain their form and relative positions, but when entering upon a curved portion of a tube some of the filaments spread out into bands of colour and cross to the inner part of the tube, travelling round its section close to the walls. If the curvature is sufficiently large or the curve sufficiently long, all the filaments would be affected. Other experiments in U-tubes seem to suggest that slipping may take place concomitant with the surface flow at the walls of the curved part of the tube. A quantity of dye having been spread over the whole of the surface of the tube, when water was allowed to flow through the tube, even at extremely low velocities, the colour disappeared immediately from the outer wall of the bend, more slowly from the inner wall, and very slowly indeed from the straight part of the tube.

In the experiments it was observed that as the velocity of flow increased there was an increase in curvature of the stream-lines. It is inferred that the resistance to flow along the tube walls from the outer to the inner wall does not vary as the velocity directly, as in the ordinary viscosity equation,

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but it varies as the velocity raised to a power n, where n is greater than 1, and probably greater than 2.

Except for the stream-lines near the walls of the tube the flow in a curved tube at low velocities appears to be in accordance with the viscosity law. The increased resistance referred to above applies to the water which has impinged upon the walls and is in its circuit along the walls of the pipe.

If a pipe is not perfectly straight, the flow for the whole section of the pipe cannot be wholly viscous flow, since associated with viscous flow there is always some surface flow, that is to say, there is "skin friction," the effect of which is to increase the resistance of the pipe and to lessen the total discharge; or, for a bent pipe, n is greater than unity in the formula $S = Kv^n/m$.

In the author's previous experiments referred to on p. 119, it was shown that the increased resistance due to curvature of a pipe was relatively greater at velocities below the critical velocity than at velocities which give turbulent motion in a straight pipe. This relatively greater resistance at low velocities is probably due to the generation of "skin friction," which would not exist in a straight pipe of the same area at the same velocity, whereas the "skin friction" already existing is merely augmented at velocities which would cause turbulent motion in a straight pipe.

Although surface flow and viscous flow may exist together in a curved pipe, it was observed that in U-tubes and in angle pipes whilst the filaments in the straight pipe before reaching the walls of the bend continued unbroken up to the usual critical velocity in a straight pipe, the filaments flowing through the straight pipe after leaving the bend usually broke up at velocities much below the critical velocity. The surface flow which commenced in the bend generated vortices which persisted in the water flowing through the outlet straight part of the pipe. This shows that the effect of a pipe bend or of an angle is not only to increase the resistance to flow in the bend itself, but also to increase the resistance in the contiguous straight pipe after the water has left the bend.

This agrees with the results obtained by investigators who have experimented on the loss of pressure in the pipe bends used by engineers.

The foregoing experiments indicate that, where it is beneficial to break up the regular lines of flow in a pipe, a curved pipe is more effective than a straight one. They show, for example, that in a tubular boiler or in a condenser of a steam engine, curved pipes would be more efficient than straight pipes, for when water is flowing at low velocity in a straight pipe, the water near the centre of the pipe section does not approach the sides during its passage through the pipe, but in a curved pipe the water is continually

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changing its position with respect to the sides of the pipe, and the water which is flowing near the centre at one part approaches the sides as it moves through the pipe, and flowing near the sides it exerts a "scouring" action on the pipe walls, thus increasing the effectiveness of the pipe surface in transferring heat.

Secondary γ-Rays produced by β-Rays.

By J. A. GRAY, B.Sc., 1851 Exhibition Scholar, University of Melbourne.

(Communicated by Prof. E. Rutherford, F.R.S. Received February 4,—Read February 23, 1911.)

When the cathode rays of a vacuum tube impinge on any material they produce the X-rays, which are not deviated by a magnetic field, and are much more penetrating than the cathode rays which produce them. We might, therefore, expect that when the β-rays from radioactive substances impinge on a plate, similar penetrating rays would be emitted from the plate. Such a penetrating type of rays, the γ-rays, is almost invariably associated with the β-rays, but it has generally been thought that these γ-rays are due to the expulsion of the β-ray from the radioactive atom. In some cases they are certainly not due to the impact of β-rays on external objects, the γ-rays of radium C being an instance of this. Here the γ-rays come from the radioactive atoms, and in such amount that they effectually mask the possible production of γ-rays by β-rays as the experiments of H. Starke* show.

Starke attempted to find whether β-rays did produce γ-rays.† He used for this purpose 6 milligrammes of radium bromide contained in a very thin glass tube, which let most of the β-rays out. The γ-rays from this ionised the air in an electroscope, the walls of which were thick enough to absorb all the β-rays. He looked for an increase in the ionisation when various materials were placed just behind the radium. He found practically no difference in the reading, and, from that and a similar experiment in which he deflected the β-rays away from the electroscope by a magnetic field, concluded that no measurable γ-radiation was caused by the β-rays of radium C.

* H. Starke, 'Le Radium,' February, 1908, p. 35.

† In this paper a distinction is drawn between primary γ-rays and secondary γ-rays. By primary γ-rays are meant γ-rays coming from the radioactive atom. By secondary γ-rays, γ-rays produced by the impact of β-rays on external materials.

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His experiments show that, if γ-rays are produced, they form a very small proportion of those coming from the radioactive atom.

Subsequently Davisson* used a different arrangement. He utilised the property of a magnetic field, which turns the path of the β-rays into spirals around the lines of force, to direct the β-rays from some radium C on to a lead plate. He found some slight but not very definite evidence of the formation of secondary γ-rays in the lead.

There are other substances, however, emitting β-rays, in which the emission of γ-rays is very weak compared with that observed in the case of radium C. Soddy and Russell† have shown that with specimens of uranium X and radium C of equal β-ray intensity, the γ-rays of uranium X are only about 2 per cent. of those from radium C. Again, Schmidt‡ found that the γ-rays of radium E produce initially only 0·016 per cent. of the ionisation caused by the β- and γ-rays from radium E in an electroscope. Meyer and Schweidler§ found a ratio 0·033 per cent., whereas in the case of the γ-rays of radium C the ratio is about 2 per cent.

Substances like uranium X and radium E are therefore much better suited for an examination of the production of secondary γ-rays. Especially is this the case with radium E, for the γ-rays, as well as being present in small quantity, are very easily absorbed by lead (see fig. 4 referred to later, p. 138). The writer, during the course of some experiments on the γ-rays from radium E, has shown that γ-rays are produced by β-rays.

The material used was a very active preparation of radium D with its products, radium E and F, and was initially used in magnetic experiments on the velocity of the β-rays from radium E.‖ It was provided by Prof. Rutherford, and had been separated from a large quantity of radium by Prof. Boltwood, preparatory to the determination of the rate of production of helium by radium by Rutherford and Boltwood.¶ The radium D was mixed with lead, which had been added to the radium to ensure the complete separation of the radium D, so that 90 per cent. of the material consisted of lead sulphate. For the magnetic experiments, it was placed in a groove in an aluminium plate, the groove being 1·2 cm. long, 0·4 mm. wide and deep. A sheet of mica was placed over the material, which for safety was hermetically sealed. Special care had been taken by Prof. Boltwood to

* Davisson, 'Phys. Rev.,' 1909, vol. 28, p. 469.
† Soddy and Russell, 'Phil. Mag.,' October, 1909, p. 620.
‡ H. W. Schmidt, 'Phys. Zeit.,' 1907, vol. 8, p. 361.
§ Meyer and Schweidler, 'Wien. Ber.,' May, 1906, vol. 115, Abt. ii a.
‖ Gray, 'Roy. Soc. Proc.,' A, 1910, vol. 84, p. 136.
¶ Rutherford and Boltwood, 'Manchester Lit. and Phil. Soc.,' 1910.

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remove all traces of radium, and an examination of the γ-rays showed that there was practically none present.

The production of secondary γ-rays by β-rays was shown in the following manner:—The aluminium plate, which was 1·25 mm. thick, 3 cm. long, and 1 cm. broad, was placed below the β-ray electroscope E (fig. 1), the active material facing downwards. Between it and the electroscope was placed a sheet of iron FE 0·6 mm. thick, a thickness sufficient to cut off the β-rays of radium E. The radiator PB was placed directly below the active matter, and any radiation coming from it had to pass through the aluminium and iron plates before entering the electroscope.

Readings were taken with and without the radiator, the difference being a measure of the secondary radiation. Using 0·135 mm. of lead as radiator, it was found that this difference was 1·25 divisions per minute, the respective readings being 5·65 and 4·40.

An absorption experiment with iron sheets, 0·6 mm. thick, showed that this radiation was not due to penetrating β-rays, and the results are tabulated below:—

Table I.

Absorber.	Reading (no radiator).	Lead radiator.	Secondary radiation.
One iron sheet	4·40	5·65	1·25
Two iron sheets	3·20	4·10	0·90
Three iron sheets	2·61	3·32	0·71

This table shows that the rays are of the same order of penetrating power as those coming from the active material. They cannot be caused by the α-rays from radium F, and are in rather too large a quantity to be scattered γ-rays from the active material, so it was thought that they were caused by the impact of the β-rays.

The following experiment differentiated between the last two probable causes. Sheets of paper were placed just below the active matter to cut off the β-rays from the lead radiator. The secondary radiation was measured as before, and the results are given in the following table:—

Table II.

Absorber of β-rays.	Transmission of β-rays by paper.	Secondary radiation.
	Per cent.	
0	100	1·25
4 sheets of paper	54	0·75
12 sheets of paper	18	0·29

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The paper can absorb very little of the γ-rays, yet it is seen that when the intensity of the β-rays is cut down to 54 per cent., the secondary radiation is reduced to 0·75, or 60 per cent. Similarly, when the intensity is cut down to 18 per cent., the secondary radiation is reduced to 23 per cent.

Most of the penetrating radiation formed in the lead plate, therefore, is due to the β-rays, the amount due to the γ-rays from the active matter being very small. A separate experiment, in which the β-rays were cut off by graphite, gave the amount as 0·10 division per minute. The β-rays thus form γ-rays in the lead plate which, passing through the aluminium and iron plates, give a reading of 1·15 divisions per minute approximately.

The formation of secondary γ-rays in other materials has been examined

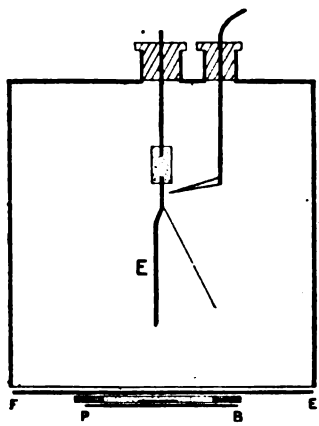

Fig. 1.

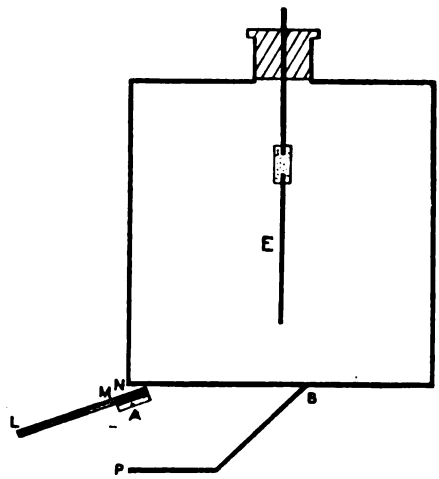

Fig. 2.

in a similar manner. The results are given in the following table, and expressed in divisions per minute of the electroscope:—

Table III.

Graphite	0·20	Silver	0·55
Aluminium	0·26	Gold	1·19
Iron	0·31	Lead	1·25

No correction has been made for the scattered γ-radiation from the active material, which is about 0·10 division. The numbers show that the secondary radiation from the "incident" side of a radiator increases with the atomic weight, being roughly proportional to it. The relative effects would also depend on the penetrating power of the radiation from different

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materials. It is probably softer the lower the atomic weight, but the effects are too small for accurate measurement.

The formation of these secondary γ-rays has been verified by other methods, in which the β-rays are turned away from the radiation by means of a magnetic field. One arrangement used is shown in fig. 2.

The electroscope E was placed above the poles of an electromagnet which gave a field perpendicular to the plane of the figure. The bottom of the electroscope consisted of sufficient aluminium and cardboard to cut off the β-rays, the rest being of iron 1 mm. thick. A lead radiator PB of section shown in the figure was placed below the active matter A and between the pole pieces, which were 10 cm. apart. The lead N absorbed most of the direct radiation from A. The cardboard LM prevented the β-rays striking the sides of the electroscope. The pole pieces were covered by cardboard. The following are the readings, M.F. referring to a magnetic field of 1000 Gauss :—

Table IV.

Disposition.	Reading.
(*a*) Radium D uncovered, no radiator	0·76
(*b*) „ lead radiator.....	1·12
(*c*) „ „ M.F. tending to turn β-rays to the left	0·77
(*d*) With the M.F. in opposite direction	0·98
(*e*) Radium D covered so as to cut off β-rays	0·76
(*f*) „ „ M.F.....	0·76

The difference between (*a*) and (*b*) gives the amount of γ-radiation entering the electroscope from the lead plate. With 5 mm. of wood, as well as the cardboard, under the electroscope, this difference was 0·32. It is seen from (*c*) that, when a strong enough magnetic field is applied to turn the β-rays away from the lead plate, this penetrating radiation is not set up. Readings (*e*) and (*f*) show that the magnetic field in itself has no effect on the electroscope reading. The experiment therefore confirms the result found by the other method.

The presence of γ-rays on the other side of a plate struck by β-rays, or emergent γ-rays as they may be called, was shown as follows:—The bottom of the electroscope E (fig. 3) consisted of 1 mm. of aluminium and 1·35 mm. of cardboard. Directly below was the radiator R. The active matter was placed between the poles N, S, and 6 cm. below R. Readings were taken with and without a magnetic field. The magnetic field was of about 1000 Gauss. The results are collected in Table V.

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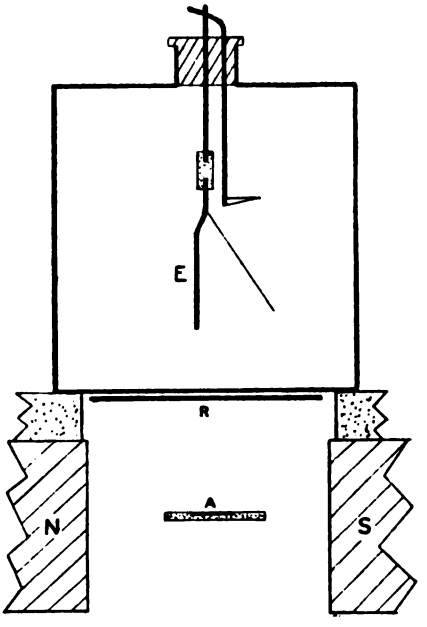

FIG. 3.

Table V.

	Radiator.	Readings.		Secondary radiation.
		Without field.	With M.F.	
1	Cardboard, 2 mm. thick	4·13	3·85	0·28
2	Aluminium, 1 mm. „	3·80	3·42	0·38
3	Iron, 0·55 mm. „	2·20	1·84	0·36
4	Lead, 0·12 mm. „	2·70	1·83	0·87
5	Lead,* 0·12 mm. „	2·09	1·37	0·72
6	Aluminium (β-rays cut off).....	3·12	3·12	
7	Iron (β-rays cut off).....	1·73	1·73	

* In this case an extra millimetre of aluminium was placed between the radiator and electroscope.

In (6) and (7) the same radiators were used as in (1) and (2), but aluminium and cardboard were placed directly above the active material to cut off the β-rays. These readings again show that the magnetic field in itself has no effect on the electroscope reading.

This table, therefore, shows the production of secondary γ-rays, the more being formed the greater the atomic weight of the radiator. In comparing (2) and (3) allowance must be made for the greater absorption of the secondary radiation in the iron. Experiments (4) and (5) show again that

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the secondary γ-rays from lead have the same order of penetrating power as the γ-rays from the active material, being, if anything, harder.

That these rays are not deflected by a magnetic field was shown in the following manner. The aluminium plate (fig. 3) was reversed so that the active material was on the lower side. Readings were taken with a lead radiator just under the active material, and are given below.

Table VI.

	Disposition.	Reading.
1	Lead radiator underneath	4·00
2	„ magnetic field of 1000 Gauss applied...	4·00
3	No radiator	3·17

The table shows that, when the radiator was present, there was no difference in the readings whether a magnetic field was applied or not, and thus, that the rays formed in the lead are not deflected by a magnetic field.

The figures for the secondary γ-radiation from lead show that the β-rays escaping from the active material produce γ-rays to the extent of 25 per cent. of the γ-rays coming from the active material used. The material with which the radium D is mixed is mainly lead sulphate. As the material is in the form of a thick layer between 0·3 and 0·4 mm. thick, only a comparatively small percentage of the β-rays can escape. There must, therefore, be a production of γ-rays in the material, mainly in the lead, comparable with that produced in a lead plate by the issuing β-rays.

These results indicate that the γ-rays ordinarily observed from a preparation of radium E may be largely, if not entirely, secondary in origin; but before coming to a definite conclusion it will be necessary to examine the γ-radiation, if any, emitted from a thin film of radium E, spread on a very thin plate of low atomic weight. Experiments in this direction are now being made. It is also intended to continue experiments with uranium X and actinium in order to test how far the γ-rays produced may be secondary in origin.

It may be of interest to compare the relative β- and γ-radiations of radium E and uranium X. Correcting for absorption in the aluminium and iron plates, the incident γ-rays from the lead radiator PB (fig. 1) would give a reading of about three divisions per minute. The β-rays producing them give a reading of 7500 per minute, the initial ionisation, then, due to the γ-rays being one part in 2500 of that due to the β-rays producing them.

It has been stated above that Soddy and Russell found that the γ-rays from a specimen of uranium X were about 2 per cent. of the γ-rays from

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radium C, the intensity of the β-rays from the two substances being equal. The γ-rays of radium C cause in an ordinary iron electroscope about 2 per cent. of the initial ionisation due to the β- and γ-rays, so that the initial ionisation due to the γ-rays from their preparation of uranium X would be about 0·04 per cent. of that due to the β-rays, or one part in 2500. This is the order one would expect from the secondary γ-rays produced by the β-rays in the platinum on which it had been placed.

The curves in fig. 4 show the results of some absorption experiments. The activity has been plotted against the mass in grammes per unit area of

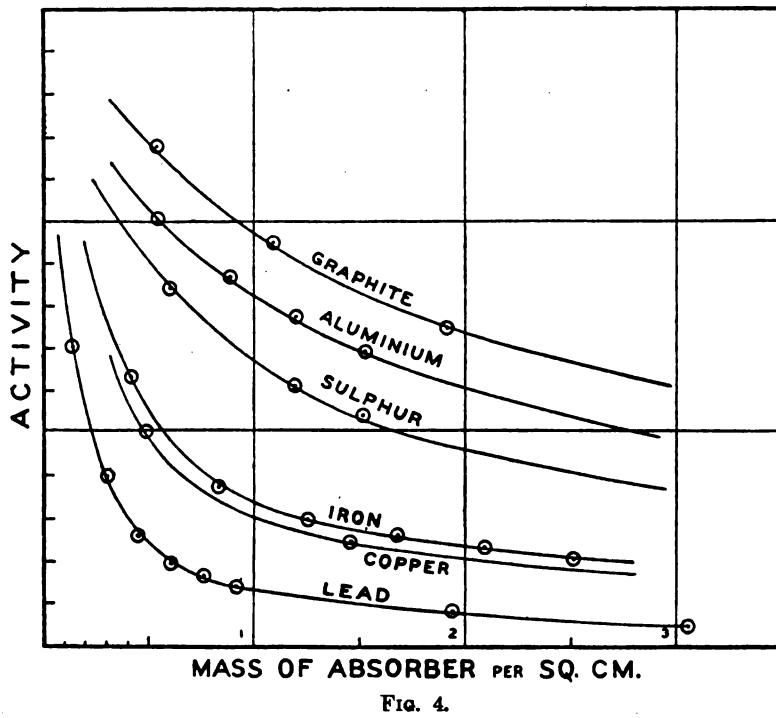

FIG. 4.

the absorbing materials. No correction has been made for the production of secondary γ-rays in the absorbing materials, but since more of these are formed in materials of higher atomic weight, this only serves to make the differences in the curves less marked (see Table V). The curves, therefore, show the much greater absorption of soft γ-rays by materials of high atomic weight than by materials of low atomic weight. In this respect the γ-rays of radium E are similar to X-rays.

The results of the experiments on the secondary γ-rays are summarised below :—

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1. γ-rays are produced by the β-rays of radium E in different materials, the greater in amount the greater the atomic weight of the material.

2. The γ-rays of radium E may be entirely secondary in nature. At all events, the γ-radiation can be greatly increased by a suitable disposition of the material and apparatus.

In conclusion, the writer wishes to express his best thanks to Prof. Rutherford for his kind interest in and advice during these experiments, and also to Prof. Boltwood for the preparation of the material employed.

On the Measurement of Specific Inductive Capacity.

By CHARLES NIVEN, F.R.S., Professor of Natural Philosophy, University of Aberdeen.

(Received February 9,—Read February 23, 1911.)

1. The discrepancy between Maxwell's theory of refraction and the values of the specific inductive capacities of some of the commoner liquids is well known, and the idea which naturally suggests itself is that the first values deduced for these capacities were obtained by using slowly alternating electric forces, and that if the period of alternation were greatly increased, a closer approximation to the values required by Maxwell's theory might be gained.

Among other methods employed is one by Thwing, founded on the principle of resonance, in which the period of the oscillations set up in a discharging circuit, which may be called the primary, is gradually altered till it agrees with the period of another fixed circuit, here called the secondary, in inductive connection with it. When the two periods are the same, it is assumed that the value of CL is the same for both, C being the capacity of one system and L the inductance of the circuit connected with it.

If we reverse Thwing's arrangement we may suppose the primary circuit fixed and modify the secondary till resonance is got. The measurements to be subsequently recorded were obtained in this way, using Fleming's cymometer as the adjustable resonator. In this way alternations were used whose frequency was comparable with a million per second, but the cymometer was only used to give comparative readings, the capacity of a

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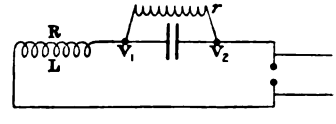
condenser with a liquid dielectric being compared with that of another with air between its plates. A diagram of the connections will be given later on when investigating the condition of resonance between the primary and secondary circuits.

Theoretically, the oscillations of a liquid condenser are complicated by the conduction which takes place through the liquid. The expression for its natural period is first found, and then the condition of resonance between it and the secondary circuit determined. This condition will be seen to be very simple in form, and reduces practically to that assumed by Thwing, viz., that CL is the same for both systems. Satisfactory determinations may be obtained in this way with liquids which are fair insulators, but if the liquid conduct to any extent, as is the case with water, alcohol, and other substances which have a high dielectric capacity, it is impossible to get it to stand up to the discharge or permit a spark to pass at all between the terminals of the circuit. To overcome this difficulty it was thought that if another condenser were put into the circuit, it might be possible to force the vibrations of the liquid condenser to take place, and this proved to be the case. The vibration period of this system is given by a somewhat complicated expression, but if the capacity of this additional condenser, introduced in series with the liquid one, be very large compared to the latter, it may be neglected, and the resulting period is that due to the liquid condenser. The additional condenser used was a battery of from three to five large Leyden jars. Its effect on the period of the discharge was tested by interposing it in the circuit of an air condenser having about the same capacity as the liquid condensers employed. It was found that the oscillation period was practically the same, whether the large condenser was introduced in series or left out altogether.

The results of some experiments made on water and alcohol are given at the end of this paper. They give values for the dielectric capacity agreeing with those found by other observers. Owing, however, to the heating effect which takes place with the large discharges used, it was found necessary to employ special means for securing that the liquid should be kept at a known constant temperature. Details of the arrangement used will be found in the paper.

2. The adjoining figure is the diagram for the discharge of a condenser



with resistance r between its plates. The wires from the terminals of the

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spark-gap lead to the secondary terminals of an induction coil, which in the experiments made was interrupted by a mercury jet revolving in coal gas. L is the inductance of the discharging circuit, R its resistance. Al the moment when the discharge passes the resistance of the spark-gap breaks down, allowing oscillations to be set up in the circuit. If V_1 and V_2 be the potentials at the terminals of the condenser, the current across the latter is $C\frac{d}{dt}(V_2-V_1)$; that carried along the resistance r is $r^{-1}(V_2-V_1)$; thus the whole current in the circuit is $\left(r^{-1}+C\frac{d}{dt}\right)(V_2-V_1)=i$.

But
$$V_1-V_2=\left(R+L\frac{d}{dt}\right)i,$$

and thus
$$\left(R+L\frac{d}{dt}\right)i+\left(r^{-1}+C\frac{d}{dt}\right)^{-1}i=0.$$

If
$$i=e^{zt},$$

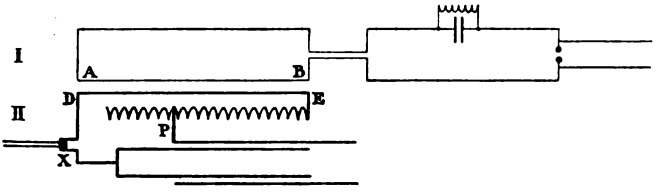
then
$$CLz^2+\left(CR+\frac{L}{R}\right)z+\frac{R}{r}+1=0,$$

the solution of which,

$$z=-\frac{1}{2}\left(\frac{R}{L}+\frac{1}{Cr}\right)\pm\sqrt{-\frac{1}{CL}+\frac{1}{4}\left(\frac{1}{Cr}-\frac{R}{L}\right)^2},$$

is mathematically of the same form as if the dielectric were perfectly insulating. The conduction through the liquid dielectric affects both the rate of damping and the period of oscillation, the former probably the most. It is unnecessary, however, to enter more minutely into a consideration of the relative magnitude of the different terms in the expression for z, because the next investigation shows that the condition for best resonance is of a much simpler form, and does not require such a discussion.

3. In the next diagram, Circuit I is that of the condenser, with inductance consisting of four turns of wire, in the form of a rectangle. Circuit II is that of the cymometer, consisting of a coil of copper wire of variable length,



and of a cylindrical condenser of variable capacity. The movable contact piece (P) varies the length of the coil introduced and the capacity of the

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condenser simultaneously, so that the ratio of the two is approximately constant. The cymometer circuit also includes a small coil (X), inside which is a thermo-electric junction, the indications of which were read by a sensitive reflecting galvanometer.

The two circuits are connected inductively by the two straight conductors AB, DE, the coefficient of induction, M, between which is very small, so that, though currents are set up which are apparent in the sensitive cymometer, their reaction on the primary system is probably entirely negligible. The currents in the primary discharging circuit are therefore still given by the equation

$$\left[\mathrm{L}\frac{d}{dt}+\mathrm{R}+\left(r^{-1}+\mathrm{C}\frac{d}{dt}\right)^{-1}\right]\mathrm{I}=0,$$

the solution of which is given by $\mathrm{I}=e^{zt}$, and the equation for z is that given in the preceding article.

If we put $z=p\pm q\sqrt{-1}$, we see that if z_1 and z_2 be the two values of z,

$$p^2+q^2=z_1z_2=\frac{1}{\mathrm{CL}}\left(\frac{\mathrm{R}}{r}+1\right).$$

The current J in the cymometer circuit is given by

$$\left(\mathrm{L}_1\frac{d^2}{dt^2}+\mathrm{R}_1\frac{d}{dt}+\frac{1}{\mathrm{C}_1}\right)\mathrm{J}+\mathrm{M}\frac{d^2\mathrm{I}}{dt^2}=0,$$

L_1, R_1, C_1 being the inductance, resistance, and capacity in this circuit; and substituting for I

$$\mathrm{J}=-\mathrm{M}z^2\mathrm{I}/(\mathrm{L}_1z^2+\mathrm{R}_1z+1/\mathrm{C}_1).$$

If we substitute for z its value $p+q\sqrt{-1}$, the denominator becomes

$$\mathrm{L}_1(p^2-q^2)+\mathrm{R}_1p+\mathrm{C}_1^{-1}+\sqrt{-1}\,.\,q\,(2p\mathrm{L}_1+\mathrm{R}_1),$$

which may be written $\Delta e^{\alpha\sqrt{-1}}$, where

$$\Delta^2=\{\mathrm{L}_1(p^2-q^2)+\mathrm{R}_1p+\mathrm{C}_1^{-1}\}^2+q^2(2p\mathrm{L}_1+\mathrm{R}_1)^2.$$

The expression for J is

$$-\mathrm{M}z^2e^{pt+(qt-\alpha)\sqrt{-1}}/\Delta;$$

its amplitude, therefore, will be a maximum when Δ is least.

In dealing with this expression, we must remember that L_1 and C_1 are approximately proportional to each other, each being nearly proportional to the distance along which the contact maker is moved from the end of the spiral, or, what comes to the same thing, from the end of the inner tube of the condenser when the other tube is drawn fully off. As regards R_1, it consists of two parts: a constant part, the resistance of the coil X, which is about 6 ohms, and a variable part, depending on the part of the spiral

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introduced, and therefore also proportional to L_1. If we call the length of the spiral employed x, we may put

$$L_1 = \lambda x, \quad C_1 = \kappa x, \quad R_1 = a + bx.$$

If, now, we seek the condition that Δ may be a minimum by the variation of x, we shall find that b always enters into the expression coupled with terms of the form $p\lambda$.

But we may estimate by measurement the resistance and inductance of the spiral per centimetre; they are approximately

$$1/90 \text{ ohm and } 4000 \text{ cm.}$$

and $p = 2\pi n$, where n may be taken about half a million. Thus $b = 10^7$ and $p\lambda = 10^{10}$ in round numbers; the variation of R_1 is therefore quite negligible. Treating it as constant, the condition for a minimum reduces to

$$\{\lambda x(p^2+q^2)+\tfrac{1}{2}R_1 p\}^2 = \left(\frac{1}{\kappa x}+\tfrac{1}{2}R_1 p\right)^2,$$

and therefore

$$L_1 C_1 = (p^2+q^2)^{-1} = LC/(R/r+1).$$

In most cases R/r is quite negligible, so that we may take for the condition of resonance

$$C_1 L_1 = CL.$$

4. The theory of a liquid condenser in series with a perfectly insulating one may now be given.

The difference of potentials at the ends of the liquid condenser is

$$V_1 - V_2 = \left(C\frac{d}{dt}+r^{-1}\right)^{-1} I,$$

that at the ends of the insulating condenser

$$V_2 - V_3 = \left(C'\frac{d}{dt}\right)^{-1} I,$$

that at the ends of the coil having inductance and resistance

$$V_3 - V_1 = \left(L\frac{d}{dt}+R\right) I.$$

Thus for the current I we have

$$\left\{L\frac{d}{dt}+R+\left(C'\frac{d}{dt}\right)^{-1}+\left(C\frac{d}{dt}+r^{-1}\right)^{-1}\right\} I = 0.$$

Putting

$$I = e^{zt},$$

we obtain

$$Lz^2+Rz+C'^{-1}+z(Cz+r^{-1})^{-1} = 0.$$

If C' be taken as infinite compared to C, this equation reduces to

$$Lz+R+(Cz+r^{-1})^{-1} = 0,$$

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the vibration period is therefore the same as if the condenser C′ were not interposed.

5. The method explained in the foregoing sections was applied to find the dielectric (or specific inductive) capacity of water and alcohol. The condenser used had the form of two concentric spheres whose diameters were respectively 9·5 (inside measurement) and 7·5 cm. Its capacity in electrostatic units was therefore 17·8, with air as dielectric. The outer sphere had two taps inserted at the top and bottom, and the lower tap was connected with a copper spiral, through which the liquid examined was allowed to flow, the whole system, spiral and condenser, being immersed in a large vessel containing water at a known temperature. When pure water, twice distilled, was run through the condenser, the cymometer reading gave a value for $\sqrt{CL}$ of 14·5, the temperature in the outer containing vessel being 0° C., being kept constant by filling it with a mixture of snow and water. This was compared with the cymometer reading for an air-leyden formed of nine plates of glass coated on both sides with tin foil over an area 25 cm. by 25 cm., and separated by small pieces of glass each 0·38 cm. thick. The capacity of this condenser in electrostatic units is therefore

$$8 \times 25 \times 25/4\pi \times 0{\cdot}38 = 1047 \text{ cm.}$$

The cymometer reading for this condenser was

$$\sqrt{CL} = 11{\cdot}7.$$

The value for K_0, the dielectric capacity of water at 0° C., is thus given by

$$\frac{K_0 \times 17{\cdot}8}{1047} = \left(\frac{14{\cdot}5}{11{\cdot}7}\right)^2, \qquad \text{or} \qquad K_0 = 90{\cdot}36.$$

By varying the temperature of the surrounding water the values of K_0 may be got at those temperatures. The following table is a record of some results thus obtained:—

Dielectric Capacity, K, of Water.

Temperature Centigrade.	Value of CL.	Value of K.	Variation for 1° C.
0	14·5	90·36	
7	13·65	80·06	
33	12·7	69·31	−0·64
59·5	11·65	58·32	−0·54
83	9·4	37·97	−0·63

Similar observations were made with alcohol as dielectric. Owing to its smaller dielectric capacity, the contact maker had to be moved further down

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the scale, and the readings are perhaps not so accurate as in the case of water. A new form of condenser with a larger electrostatic capacity with air would have been preferable. The following were the results obtained with this substance:—

At 12° C. ..... K = 24·5
„ 64°·2 C. ..... K = 16·0

giving a variation between 12° and 64° of −0·161 per 1° C.

I have pleasure in acknowledging the assistance which I received from Mr. A. E. M. Geddes, B.Sc., in conducting the above experiments.

Note on the Electrical Waves occurring in Nature.

By W. H. Eccles, D.Sc., A.R.C.S., and H. Morris Airey, M.Sc., F.R.A.S.

(Communicated by Sir A. W. Rücker, F.R.S. Received February 10,—Read March 9, 1911.)

It has often been pointed out that whenever a lightning discharge occurs between a cloud and the earth, or between two charged clouds, it must give rise to a violent disturbance of the local electrical field, which will spread outwards as an electric wave from the region of the discharge. A lightning discharge may be aperiodic or oscillatory; accordingly a solitary wave or a train of waves, as the case may be, travels in all directions from the centre of discharge till its energy is dissipated by divergence into space or by the absorption of the atmosphere, and thus the disturbance may reach great distances.

In wireless telegraphy these vagrant waves are a source of great trouble to the telegraph operator. Being often very intense pulses or trains they frequently set the receiving antenna, whatever its natural period may be, into more violent vibration than do the signals being listened for, and not infrequently they compel the complete suspension of traffic. By those engaged in wireless telegraphy, all these and similar disturbances are called, variously, "atmospherics," "strays," "statics," or "X's." When the usual telephonic method of receiving the Morse dots and dashes is employed, the strays are heard in the telephone as sharp clicks, as rattling noises, or as prolonged grinding or fizzing sounds. There is no doubt that some of these noises are due to other causes than vagrant waves. For example, it is well

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known that wind-driven hail, snow, or rain, produce in an earthed antenna transient currents that can affect the resonant circuits and the telephone of the receiving apparatus, and other very local causes are conceivable. But the travelling waves mentioned above, it has sometimes been surmised, form a considerable proportion of the strays heard on any occasion. It is the purpose of the observations described below to settle whether the proportion of strays due to vagrant waves of distant origin is indeed of importance. If it is, then the general properties of these waves, the limits of distance through which they can travel, and their meteorological significance (if any), all seem worthy of investigation. The particular point we are here enquiring into does not seem to have been investigated before. The sum total of the work published on the whole subject is very small, and no investigations specially directed towards the discrimination of the various causes are known to us.

The study of these natural electric waves was begun by Popoff shortly before the rise of practical wireless telegraphy. In 1895 Popoff* made use of a long vertical conductor (such as a lightning rod) in combination with a coherer in order to follow the motions of lightning storms through the atmosphere. A filings coherer was used and was automatically tapped back after registering the effect of each lightning stroke. In 1898 Boggio Lera† improved on Popoff's apparatus as regards sensitiveness, and arranged that feeble and strong disturbances should be recorded separately. His experiments with this apparatus in 1899 showed that the approach of electrical storms was heralded by frequent operation of the apparatus several hours in advance of their arrival in the locality of the observing station. These results were confirmed by Tommasina‡ in 1900, using his carbon auto-coherer. In 1901 Fenyi§ showed that the thunderstorms occurring within a radius of 100 kilometres of his station at Kaloska, Hungary, were all recorded by his coherers. Finally, Turpain,‖ in 1903, made a long series of observations that proved the possibility of utilising these radio-telegraph apparatus and methods in the forecasting of thunder weather for hours and even days in advance. We may remark at this point that the occurrence of numerous strays at a particular station is not necessarily followed by a thunderstorm in the locality—the storm may pass wide of the station. As a fact there are few days at any wireless telegraph station without its

* Popoff, 'Journal of Russian Physico-Chemical Soc.,' 1895, vols. 28—29, p. 899.

† Boggio Lera, 'Atti della Accademia Gioenia di Scienze di Catania,' January, 1900.

‡ Tommasina, 'Comptes Rendus,' November 25, 1900.

§ Fenyi, 'Comptes Rendus,' January 27, 1902.

‖ Turpain, "La Télégraphie sans Fil," p. 314.

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burden of strays. Whether these are due to very distant lightning strokes, or to extra-terrestrial causes, is a problem as yet unsolved, and is indeed one of the points to whose elucidation our own observations are tending.

The plan of attack adopted by us in these preliminary experiments was as follows:—One of us in London, and the other in Newcastle, arranged receiving apparatus just as for the telephonic reception of wireless telegraph signals. Then we listened, at times agreed upon, to the strays that happened to be audible. We recorded the principal atmospherics by an agreed system of pencil marks on paper which was ruled so that 6 inches represented a minute, each stray being recorded in its proper position on the paper by aid of the seconds hand of a watch. The period of recording was about half an hour, and was usually arranged so as to terminate or begin at or near a time when a regularly working long-distance transmitting station, such as Poldhu, Norddeich, or the Eiffel Tower, started or finished its signals. The time signals from the two last-named stations proved exceedingly useful. In this manner a fairly perfect time correlation was established between the records made by the two observers. The observers exchanged "carbon" copies of their records, and made independent comparisons of them. Fig. 1 is a reproduction of a portion of such hand-made records

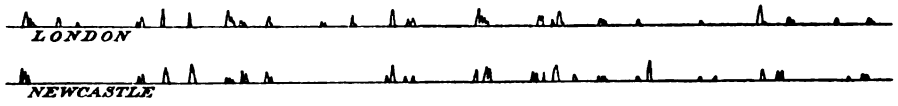

Fig. 1.

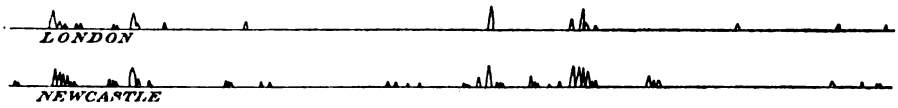

Fig. 2.

obtained on a day when there were many loud strays; fig. 2 shows records of a less crowded day. It should be explained that the height of the mark above the datum line represents the intensity of the sound in the telephone as judged by the ear of the observer. The record may be described as a rough endeavour to chronicle graphically the strength of the strays as ordinates with the time as abscissæ.

A comparison of the records shows that many of the marks made by the two observers coincide in time and, besides, bear a strong likeness to one another. Other marks, again, bear great likeness, but are recorded as belonging to slightly different instants of time. This last remark gives point to the principal weakness of the method, namely, that large errors may be

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made by each of the observers in deciding quickly the exact point of the axis of time at which to make the mark representing a stray. In consequence, reasonable allowance must be made for these personal equations in counting the number of coincidences.

Table I is a summary of our results. This table gives the total number of strays recorded in London (M), the total number in the same time at Newcastle (N), and the number of coincidences (C_1) between marks that possess a decided similarity. The column headed "Percentage of coincidences" gives the percentage proportion that the number of coincidences

Table I.

Date.	Duration of record, in seconds.	London. M.	Newcastle. N.	Coincidences. C_1.	Percentage of coincidences.
1910.					
July 26.....	560	57 (1000)	52 (2000)	27	52
„ 26.....	640	62 (2000)	53 (2000)	26	49
„ 26.....	540	46 (2000)	50 (1000)	20	44
Aug. 24.....	1360	293 (2000)	382 (2700)	227	77
„ 25.....	1680	293 (2700)	353 (2700)	197	67
„ 26.....	1720	282 (2700)	420 (2700)	205	73
„ 31.....	895	184 (40 ')	196 (2700)	106	58
„ 31.....	660	158 (2700)	160 (2700)	98	62
Sept. 1.....	955	175 (6000)	245 (2700)	122	74
„ 1.....	665	120 (2700)	185 (2700)	96	74
„ 8.....	840	96 (2000) (2800)	234 (600)	72	75
„ 8.....	780	102 (2000) (2800)	210 (2700)	72	71
„ 9.....	1660	300 (2700)	346 (2700)	191	64
„ 14.....	1652	356	470 (2700)	289	81
„ 16.....	980	229 (6000)	299 (2700)	151	69
„ 16.....	603	105 (2700)	177 (2700)	67	65
„ 22.....	1700	331 (2700)	312 (2000)	204	65

Bracketed numbers refer to the wave-length expressed in metres.

bears to the smaller of the two numbers M or N. The figures in brackets show in metres the wave-lengths to which the receiving apparatus was tuned at each station. From these latter figures it will be seen that both the antenna and its associated resonant circuit at one station were normally tuned to the same wave-length as the two circuits at the other station, but sometimes the antenna and resonant circuit at one station were tuned to a wave-length different from those at the other station, and on a few occasions the antenna and resonant circuit at one and the same station had different wave-lengths. Broadly speaking these differences in the adjustments of the receiving apparatus had little perceptible effect on the number of coincidences afterwards found in the records, which indicates that the vagrant waves come in very short trains or as solitary waves.

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To meet a possible objection to the above method of analysing the records, we give in Table II the results of analysing in a manner which purposely takes no cognisance of the fact that strong resemblances exist between individual strays. Let T be the duration of the record at both stations in seconds, and suppose that M/T and N/T are small compared with unity, then the chance of one of the M marks falling within a time L/2 on either side of any assigned mark is LN/T. This being true of every one of the M marks, provided that the time L rarely includes two of the M or of the N marks, the probable number of coincidences in a random distribution of marks is therefore LMN/T, a "coincidence" being defined as the occurrence of two marks with a time L/2 or less between them. Now, if any of these coincidences are due to the operation of the same cause, as, for example, a distant lightning flash, these ought to be excluded from the application of the above formula. Let their number be X. Let the number of observed coincidences be C. Then the chance coincidences are C−X. But the random marks are M−X and N−X respectively; and by the above formula the chance coincidences are in number L(M−X)(N−X)/T. Equating this to C−X, we get the quadratic equation,

$$X^2+\{T-(M+N)\}X-(CT-MN)=0.$$

This has a positive root, which is the probable number of atmospherics due to the same lightning stroke or discharge. The number thus obtained is offered merely as a rough estimate; the assumptions on which the formula is obtained are, of course, not strictly fulfilled.

In Table II, the results of applying the formula are set out. There are columns headed C and X that did not appear in Table I. The latitude L

Table II.

Date.	Duration of record, in seconds.	London. M.	Newcastle. N.	Coincidences. C.	X.
Aug. 24.....	1660	293	382	254	249
„ 25.....	1680	293	353	220	212
„ 26.....	1720	282	420	218	210
„ 31.....	895	184	196	108	100
„ 31.....	660	158	160	101	96
Sept. 1.....	1620	295	430	224	213
„ 2.....	1620	347	334	152	121
„ 8.....	1630	198	444	149	137
„ 9.....	1660	300	346	201	189
„ 14.....	1590	356	470	294	287
„ 15.....	1650	349	337	189	171
„ 16.....	1628	334	476	231	211
„ 22.....	1695	331	312	235	230

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allowed in counting coincidences was 1 second. It will be seen that almost the same conclusions are reached by this method of analysis as by the method of counting only strays whose graphs display some resemblance.

All the above observations, excepting those of July 26, in Table I, were made during the half hour between 12.30 midnight and 1 A.M.; those of the date named were made between 10.30 and 11 A.M. From a large number of forenoon observations, such as those of July 26, we concluded that it was best to work at night. This fact may be in some part due to the "strays" produced, possibly, by electric trains and trams or other local users of large currents. Neglecting these daytime observations, the conclusion to be drawn from the above tables of results is that between 60 and 80 per cent. of the atmospherics audible at Newcastle and London, about 270 miles apart, are due to the same cause. This cause is probably a discharge of atmospheric electricity at places whose distances from the stations are possibly of the order of several hundreds of miles. We consider that these preliminary experiments are sufficiently encouraging to justify our extending the work by adopting automatic recording apparatus and by enlisting the aid of other wireless telegraph stations.

The Newcastle observations were made partly at the Armstrong College and partly at Cullercoats.

We take this opportunity of thanking the authorities of the Amalgamated Radio-Telegraph Company for permitting us to use their Cullercoats station for the purpose of the experiments described in this communication.

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A Theory of the Chemical Action of the Electric Discharge in Electrolytic Gas.

By Rev. P. J. KIRKBY, Fellow of New College, Oxford.

(Communicated by Prof. J. S. Townsend, F.R.S. Received October 13,— Read November 24, 1910.)

Introduction.

In some previous papers* experiments have been described establishing various results when an electric discharge passes through a mixture of hydrogen and oxygen at low pressures. The results, which were very complicated, suggested a theory which satisfactorily explained them and throws a light upon the manner in which chemical effects are brought about by an electric discharge.

The experiments to be recorded in the present paper were undertaken with the object of testing the theory further and of providing data for developing it. But before describing the new experiments it will probably be useful to sketch the results of the previous experiments.

In the first place, explosive gases do not explode even partially when their pressure is below a certain value which naturally varies† with the gas. That value in the case of electrolytic gas lies between 40 millimetres and 80 mm. When the pressure is less than 40 mm. and an electric discharge is passed through the hydrogen and oxygen the gases begin to combine with great regularity. The amount of the chemical action, *i.e.* the mass of the water vapour formed, is proportional to the quantity of electricity passed through the gaseous mixture, so long as the circumstances of the discharge, including pressure, current, and the distance between electrodes, are constant. This result, which bears only a faint resemblance to Faraday's law of electrolysis, has nothing apparently in common with the law of mass action, for the rate of formation of the chemical product of a given current, instead of always increasing with the concentration, can under certain conditions be absolutely diminished by greatly increasing the pressure. In addition, the chemical action is independent of the nature of the electrodes and is not confined to their neighbourhood but takes place at all points of the discharge.

* P. J. Kirkby, 'Phil. Mag.,' February, 1904, January, 1905, March, 1907.

† Thus Mr. J. E. Marsh and the writer have recently found that azoimide explodes at above 10 mm., but not much below that pressure.

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Chemical Activity Defined.

In the case of a steady long cylindrical discharge between two parallel plate electrodes, very different chemical effects are produced by the different parts of the discharge. It seems necessary here to introduce a new expression in order to describe them. Let P be any point in the discharge, and let two planes be imagined parallel to the electrodes, one containing P, the other a very short distance h from the first plane. Then the mass of the chemical product,* one only being assumed, formed after unit quantity of electricity has crossed (between the electrodes and therefore) between the planes divided by h will be called in this paper the *chemical activity at the point P.* More briefly, the chemical activity at a point may be defined as the mass of the chemical product resulting from the flow per cm. of unit quantity of electricity past the point; and this varies from point to point. The line-integral of this quantity between the electrodes, *i.e.* the mass of the chemical products resulting from the passage of unit of electricity between the electrodes, will be called the *total chemical activity* of the discharge.

The chemical activity is far greater near the cathode† than at any other point of the discharge. Across the cathode fall the total activity is nearly constant,‡ being independent of the pressure and electrodes (size and material). The chemical activity diminishes as the point recedes from the cathode; and at a distance of about 1 or 2 cm., when the gas is at a few millimetres pressure, it is scarcely appreciable§ until the positive column‖ is reached.

At points within the positive column the chemical activity is constant or very nearly constant.¶ Now the positive column can be lengthened** without appreciably changing any other circumstance of the discharge,

* In the case of electrolytic gas nearly, but not quite, the whole of the chemical product of the discharge is water. For after two-thirds or three-quarters (according to the nature of the electrodes) of a given mass of the gas was formed into water under an electric discharge, the water being absorbed by P_2O_5, the union of the remainder under the discharge showed signs of departing from the laws which related to pure electrolytic gas ('Phil. Mag.,' January, 1905, p. 183). This leads to the conclusion that at least 95 per cent. of the chemical product is water.

† P. J. Kirkby, 'Phil. Mag.,' March, 1907.

‡ 'Phil. Mag.,' January, 1905.

§ These results are deduced from the curves given, 'Phil. Mag.,' March, 1907.

‖ The "positive column" is that region of a fairly long discharge where the electric force or potential-gradient is constant or nearly constant. It is easily recognised by the eye as a long more or less luminous cylinder, sometimes striated, of a colour peculiar to the gas. It extends from a distance (varying with pressure) of several centimetres from the cathode up to the anode. Thus at a pressure of 1 mm. it begins at about 7 cm. from the cathode.

¶ 'Phil. Mag.,' March, 1907.

** *Ibid.*, and 'Phil. Mag.,' April, 1908.

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namely, if the electric force in the column is Y volts per centimetre and it is desired to increase the length of the positive column by d cm., it is merely necessary to increase the distance between the electrodes by d cm. and to add Yd volts to the battery, and with no other change the discharge will be the same as before, except that the positive column will be d cm. longer. Hence it is possible to deduce the chemical activity of the positive column by estimating the amounts of the chemical products produced by passing unit quantity of electricity through the gas by two separate discharges, passed at the same pressure, and differing only in the length of their positive columns, and then by dividing the difference in amount of these two chemical products by the difference of the lengths of the two positive columns. The result will be the chemical effect per centimetre of the positive column per unit quantity of electricity passed through it, or the chemical activity at any point of the positive column.

The chemical activity of* the positive column presents some striking features. It does not always increase with the pressure. Thus from previous experimental results† it proved to be twice as much for the pressure 1·4 mm. as for the pressure 4·5 mm. In fact the paradoxical result that the same current, passed for the same time, in hydrogen and oxygen can under certain conditions produce a greater mass of water when the pressure has certain values than when the pressure is much greater than those values is, perhaps, entirely due to the reactions within the positive column.

All these effects which are purely experimental have been accounted for by the theory suggested by the writer in previous papers,‡ namely, that the ions which constitute the electric current dissociate into uncharged atoms those molecules of the gas which they strike with adequate velocity and under favourable conditions, and that the atoms rearrange themselves according to dynamical and chemical necessities.

This theory can be tested and developed when the chemical activity is known of a uniform current flowing in various uniform fields of force through combining gases at different pressures, and such a field exists in the non-striated positive column of a long cylindrical discharge. It would of course be preferable to dispense with a gaseous discharge if it were possible to measure the chemical effects of such currents as can be made to pass in a uniform field of force without disturbing the uniformity of the field, such

* *Of* is used as an abbreviation for *at any point of* in the case of the positive column, with the understanding that the chemical activity is constant throughout it, analogously with the expression "potential *of* a conductor."

† 'Phil. Mag.,' March, 1907.

‡ 'Phil. Mag.,' February, 1904, etc.

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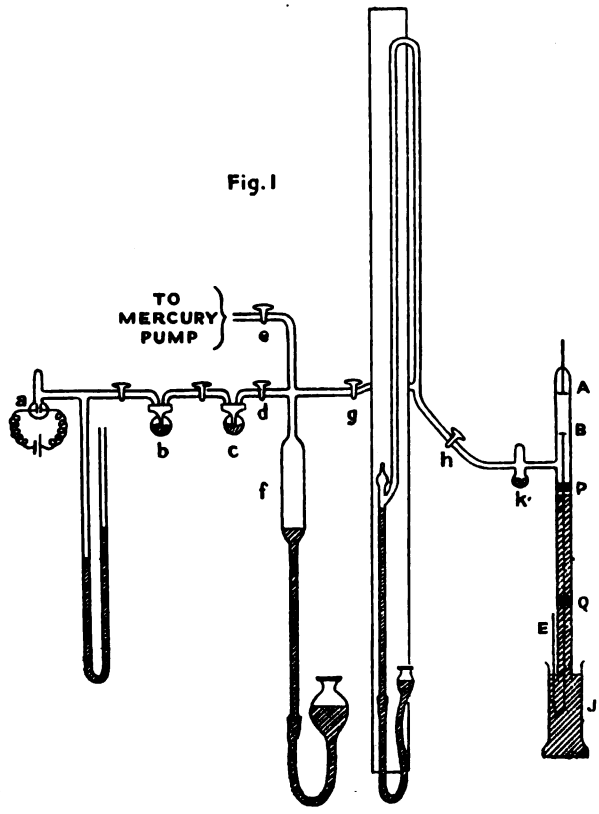
as those produced by means of the Röntgen rays or ultra-violet light. But the chemical effects of the latter kind of currents would be far too small to be detected. Hence, in order to obtain experimental data, it has proved necessary to determine the chemical activity of the positive columns of various discharges.

Thus the experiments recorded in this paper chiefly deal with positive columns and were undertaken to determine simultaneously both the chemical activity and the electric force within positive columns corresponding to different currents and pressures.

The Apparatus.

The scheme of the apparatus is shown diagrammatically in fig. 1. The mixed gas ($2H_2+O_2$) was generated in the closed vessel *a* by the electrolysis

Fig. 1



of pure barium* hydrate, was then dried over phosphorus pentoxide in the drying vessel *b* and again in *c*, and was then passed into the discharge-tube

* Gas thus prepared is remarkably pure. H. B. Baker, 'Trans. Chem. Soc.,' 1902, vol. 81.

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ABP. The latter, which was designed to permit the motion of the anode B (the cathode A was fixed), was a long vertical glass tube, about 2·4 cm., inner diameter, supported in a jar J full of mercury. Fig. 1 shows the tube partly filled with mercury, as it was during the experiments, which were all made at low pressures (less than 2 mm.). The distance of the top of the mercury from the cathode A, a distance which varied of course with the barometer, was then about 40 cm. The anode B was supported by a stout steel rod which passed through the fixed steel guides P, Q, and, bending round in the mercury of the jar J, terminated at E. Thus B could be raised or lowered by raising or lowering E.

Both electrodes were made of pure silver faced with a layer, 0·25 mm. thick, of pure gold and were intended to prevent oxidation with its disturbing effects. They were made by Messrs. Johnson and Matthey, of Hatton Garden. The anode, which had to move freely along the tube, was 2 cm. in diameter, while the fixed cathode was rather larger, fitting fairly close to the tube.

The side-tube by which the gas entered the discharge-tube was fused to that tube below the lowest position of the anode, so that the uniformity of the discharge might not be disturbed; and, being short and comparatively wide, it permitted the water vapour formed by the discharge to diffuse rapidly to the phosphorus pentoxide contained in the little glass vessel k to which its other end was fused. The object of the tap h on the other side of k was to prevent the water vapour escaping before coming in contact with the phosphorus pentoxide. When h was opened the McLeod gauge shown in fig. 1 and an ordinary manometer, not shown, became connected with the discharge-tube ABP.

The tap g was inserted to cut off the discharge-tube with the McLeod gauge and manometer from the test of the apparatus; for the quantity of the chemical product resulting from the discharge was measured by finding the fall of pressure produced by the discharge, and it was important to increase this effect by reducing the space where the pressures were measured.

The large tube f, which could be filled with mercury, was added to the apparatus for the purpose of making accurate adjustments of the pressure in the discharge-tube.

Since the method, as will appear below, essentially involves the determination of *differences* of small pressures, it was of primary importance to measure the pressures with the utmost accuracy. For this purpose the McLeod gauge was fitted with an arrangement for raising or lowering the reservoir of mercury with a slow screw motion after rough adjustment, and a mirror was placed beside the zeros of the gauge, so that with the help of a lens the level of the mercury could be raised accurately to the zero without

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errors of parallax. In this way small pressures could be read to about 0·001 mm.

The electrical connections are shown diagrammatically in fig. 2. Z was a battery of 1700 volts or less, and R was sometimes as much as 3 megohms.

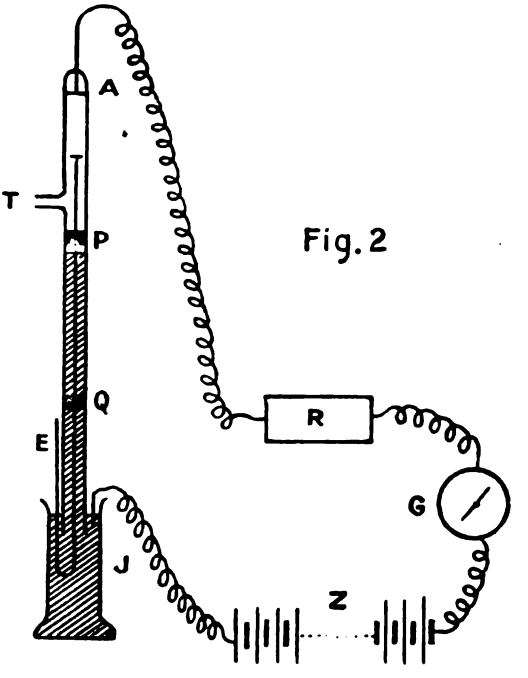

Fig. 2

G was a D'Arsonval galvanometer such that the current corresponding to a deflection of the spot of light through about 67 mm. was 10^{-4} ampère, which was the order of the currents used (see Table I).

Method of Experiment.

The hydrogen and oxygen having been introduced and the anode fixed at a certain distance, usually about 30 cm., from the cathode, the pressure was adjusted and carefully determined. A steady current C of the order 10^{-4} ampère, but otherwise arbitrary, was then passed between the electrodes for a few seconds t (between 5 and 12). Such small currents as this were necessary, for in order to extend previous results it was necessary to work with lower pressures than had hitherto been used, pressures even so low as 0·2 mm.; and larger currents, on account of their greater chemical effects, would not have remained approximately constant for a time long enough to measure accurately with a stop-watch. Another great advantage in working with very small currents is that the positive column is free* from striæ

* This does not appear to have been noticed before.

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when the current is below a certain value, at least in the case of low enough pressures, and in the absence of striæ the field of force within the positive column is quite uniform.

The effect of the passing of the current is that water vapour is formed which diffused to, and was absorbed by, the phosphorus pentoxide in the vessel to the left of the tube T in fig. 2. This diffusion takes place very rapidly at low pressures, so that the water vapour was quickly removed. After a short interval, then, to permit of this diffusion, the pressure was again very carefully determined. The mean of the initial and final pressures was taken as the pressure p of the observed effect and the difference, Δp, between the initial pressure and the final pressure measures the chemical action produced by the passage of the Ct units of electricity through the gas. Thus $\Delta p/Ct$ or $\Delta p/\Delta Q$, the fall of pressure per coulomb, is obtained.

During the discharge the distance from the cathode of the point where the positive column began was noticed; and for the second experiment the anode was moved about d cm. nearer, d being rather less than the length of the positive column in the first discharge (and usually about 20 cm.), so that for the second experiment the positive column was very short. The pressure was then readjusted so that approximately the same mean pressure p might result for the second discharge as for the first, and the battery was also diminished from (say) Z_1 to Z_2, so that the same current might pass as before. Thus everything was the same for the two experiments except the voltage of the battery and the distance between the electrodes. After the passage of the current for the second time, $\Delta p/\Delta Q$ was again determined as before.

The difference between the two values of $\Delta p/\Delta Q$ divided by d is obviously the fall of pressure per coulomb passed through 1 cm. of the positive column in question at the pressure p, and hence is proportional to the chemical activity of the positive column; and the electric force Y in the particular positive column is simply the difference of voltage of the battery in the two cases, namely, $Z_1 - Z_2$, divided by d.

The first of these two observations, as already stated, was made with arbitrary current C; but in the second experiment with diminished distance between electrodes the same current had to be accurately reproduced in order to determine the correct value of Z_2. In practice this result is easily achieved by means of two observations with slightly different batteries giving two currents, one less, the other greater, than C, and by interpolation. Such precautions would be unnecessary if the electric force were known and only the values of $\Delta p/\Delta Q$ were required, for the latter changes but little with

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the current when the positive column is very short, as Table I below shows.

In many cases a third value of $\Delta p/\Delta Q$ was obtained with the distance between the electrodes the mean of the previous distances and the same pressure and current as before. Its value ought to be the mean of the previous values, since the positive column contributes to the total chemical effect an amount proportionate to its length. It was determined as a verification of the other two values and will help to indicate their accuracy, but was not used in deducing the chemical activity of the positive column.

Results of the Experiments.

The values of $\Delta p/\Delta Q$, determined in the manner just described, with two or more different distances D between the electrodes, but the same current C, are given in Table I for various pressures.

The significance of $\Delta p/\Delta Q$ depends of course upon the cubical capacity of the part of the apparatus where the falls of pressure produced by the current took place, viz., the part to the right of the tap *g*, fig. 1. This capacity was 474 c.c., or rather it varied within about 1·3 per cent. of this value, changing slightly with the barometer and with the length of the rod supporting the anode above the mercury. It is, however, convenient to express the results absolutely, *i.e.* independently of the apparatus. This might be done by multiplying $\Delta p/\Delta Q$ by 1000/474 so as to give the fall of pressure per coulomb that would take place in an apparatus of capacity 1 litre. But the simplest course, in view of the subsequent discussion, is to find how many molecules of water vapour* are formed by the passage through the gas of the atomic quantity of electricity, namely, the charge carried by a negative ion. This number is denoted by W. Now it is easy to show that approximately

$$W = 1{\cdot}69\,\frac{\Delta p}{\Delta Q}.$$

For if N is the number of molecules in 1 c.c. of gas at 760 mm. pressure and 15° temperature, and e the charge on an ion in electrostatic units, $Ne = 1{\cdot}22 \times 10^{10}$.† And in this apparatus of 474 c.c. a fall Δp of the pressure of electrolytic gas is due to the disappearance of $N \times 474 \times \Delta p/760$ molecules of $2H_2 + O_2$ and so to the formation of two-thirds that number of molecules of water vapour; while ΔQ coulomb is $\Delta Q \times 3 \times 10^9/e$ times the atomic (or electronic) charge. Hence the number of molecules of water formed by the

* It is assumed that any other product of the discharge than water vapour is negligible. See the third footnote to this paper.

† Townsend, 'Phil. Trans.,' A, 1899.

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passage of the atomic charge between the electrodes (W) is immediately found to be $1{\cdot}69\Delta p/\Delta Q$.

The values of W are given in Table I. Now if the least value of W corresponding to a certain pressure and current in Table I is subtracted from the greatest, and the result divided by the difference of the two values of D, it is clear that the quotient is the number of molecules of water resulting from the passage of the atomic charge through 1 cm. of the positive column. This number is denoted by w. Now the chemical activity of the positive column is the mass of the chemical product per unit length of the column and per unit quantity of electricity that passes. Hence w is proportional to the chemical activity of the positive column, and is in fact *equal* to it if the molecule of water vapour is taken as the unit mass and the atomic charge as the unit of electrical quantity. Similarly W will measure, or equal, the total activity of the discharge.

The values of w thus calculated, corresponding to the positive columns of various discharges which are fully defined by the pressure and current stated, are given in Table I in the sixth column.

The corresponding values of the electric force (Y) within the positive column are given in Table I. They were all determined by direct experiment simultaneously with w, except in one case, where Y was found for a slightly different value of p, and a correction had to be made. Although in general Y is a function of the current as well as of p, yet the currents of Table I are so small that Y is practically a function of p only. This is proved by fig. 3, in which the points determined by plotting Y against p determine a curve accurately. This curve has proved a useful check upon the values of Y, and has supplied one missing value as already alluded to. Still it is important to determine Y by direct experiment, instead of relying upon the graph, in case anything may occur to disturb the normal value of Y, as in one case corresponding to $p = 1{\cdot}4$, where the point determined by p, Y, does not fall upon the curve of fig. 3.

The values of w/p, Y/p, are given in Table I for reasons to follow. The last column of the table shows where the positive columns were observed by the eye to begin; these observations decided the least value of D, which had to exceed the distance of the beginning of the positive column from the cathode.

The rather complicated notation-symbols which it has been necessary to employ are here collected and once more fully explained for the purpose of reference.

The reason why so many observations were made with pressures near to 1·4 mm. will be given later. One result must be noticed here, namely,

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Table I.

p.	C × 10^3.	D.	$\Delta p/\Delta Q$.	W.	w.	Y.	w/p.	Y/p.	q.
1·98	0·474	24	17·2	29·1	1·24	32·5	0·63	16·4	6·5
		16	10·7	18·1					
		8	5·5	9·3					
1·75	0·44	31·5	21·0	35·5	1·12	31	0·64	17·7	
		6·5	4·4	7·4					
1·67	0·428	30	20·5	34·6	1·17	30·9	0·70	18·5	6·5
		19	13·1	22·1					
		8	5·2	8·8					
1·4	0·315	24	13·85	23·4	0·93	25	0·66	17·9	
		8	5·07	8·57					
1·4	0·257	25	19·5	32·9	1·33	27·3	0·95	19·5	6·5
		16	11·7	19·8					
		7	5·3	8·95					
1·32	0·358	25	17·4	29·4	1·18	27·4	0·90	20·8	
		7	4·8	8·1					
1·28	0·274	25	17·1	28·9	1·14	26	0·895	20·3	6·5
		16	11·7	19·8					
		7	4·9	8·3					
1·21	0·227	28	21·5	36·3	1·32	25·5	1·09	21·1	
		8	5·9	10					
1·06	0·285	31·5	21·3	36	1·13	23	1·07	21·7	7·0
		19·5	13·3	22·5					
		7·5	5·2	8·8					
0·88	0·172	31·5	20·2	34·1	1·07	21	1·22	23·9	
		8·5	5·6	9·5					
0·6	0·133	31·5	19·3	32·6	1·03	17	1·72	28·4	8
		8·5	5·3	9·0					
0·48	0·098	31·5	18·1	30·6	0·98	15·3	2·04	31·9	8·3
		10·5	5·9	10·0					
0·35	0·123	31·5	16·5	27·9	0·90	12·3	2·56	35·2	
		21	10·3	17·4					
		10·5	5·4	9·1					
0·291	0·119	31·5	15·6	26·4	0·82	11·3	2·82	38·9	10·5
		21·5	10·6	17·9					
		11·5	5·9	10·0					
0·242	0·094	31·5	13·8	23·3	0·68	10·5	2·82	43·4	10·5
		11·0	5·5	9·3					
0·193	0·106	31·5	13·1	22·1	0·65	9·6	3·37	49·7	
		11·5	5·4	9·1					

NOTATION OF TABLE I.

p = the mean pressure during the discharge in millimetres of mercury.

Δp = the fall of pressure produced by the discharge.

C = the current of the steady discharge in ampères, so that the second column gives the current in milliampères.

ΔQ = the quantity of electricity in coulombs passed through during the discharge (Ct).

D = distance between the electrodes.

W = the number of molecules of water produced by the passage of the atomic quantity of electricity between the electrodes = 1·69 × $\Delta p/\Delta Q$ = the total chemical activity of the discharge.

w = the difference of the greatest and least values of W divided by the difference of the corresponding values of D = the chemical activity of the positive column.

Y = the electric force (volts per centimetre) of the positive column.

q = the distance from the cathode of the nearest part of the positive column.

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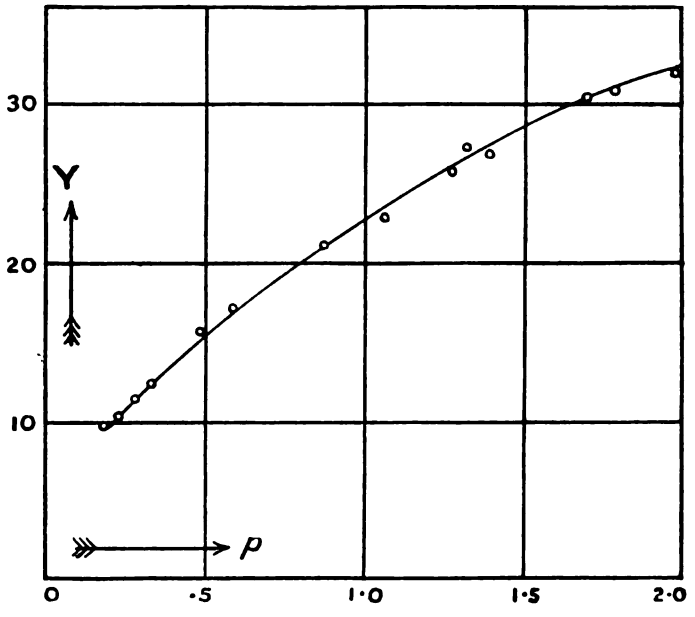
Fig. 3



the two discrepant values of w corresponding to the same pressure 1·4 mm. This discrepancy lies far beyond the errors of observation, but is fully explained by the concomitant discrepancy in the values of Y, which is possibly the effect of the presence of water vapour. In fact each value of w is related to the corresponding value of Y in the manner required by the theory within the limits of experimental error.

Limits of Experimental Errors.

The errors involved in the various values of $\Delta p/\Delta Q$ and therefore of W were in most cases probably less than 5 per cent. The largest values corresponding to the largest values of D when repeated seldom differed by more than that, and sometimes the agreement was much closer. If the same order of error is assumed in the least values of W, which are a small fraction (generally about one-third or one-fourth) of the greatest values, the values of w, which depend on the difference of greatest and least values, would have a rather greater error-limit, 7 or 8 per cent., or even more in a few cases.

Deductions from Table I that are Independent of Theory.

If the values of w/p given in the table are plotted against the corresponding values of Y/p, the points so obtained determine a simple continuous curve. This is shown in fig. 4.

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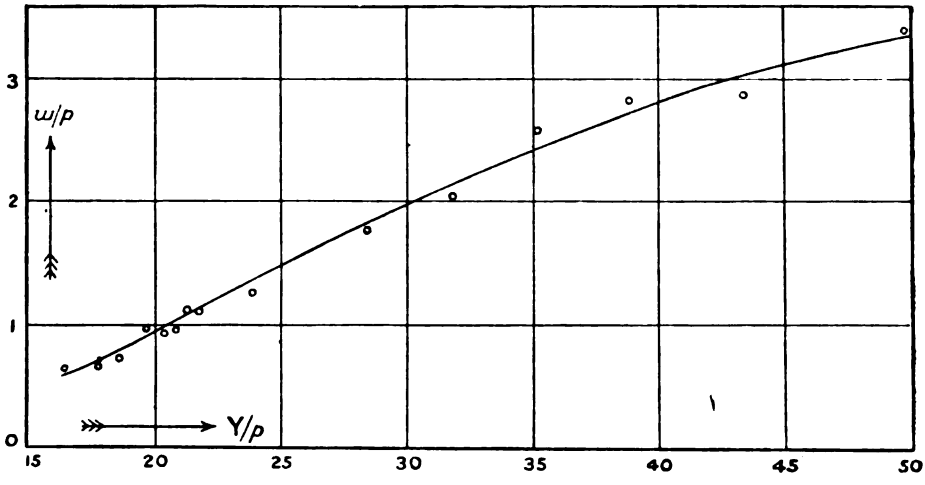
Fig. 4



It follows that w/p is a function of Y/p, and that the relation between these two variables is *independent of the current*, for the current was arbitrary and varied by several hundred per cent., while the points plotted in fig. 4 fall upon the curve within the limits of experimental error.

This result proves definitely that the observed chemical effects in the positive column are not directly due to recombination* of ions, for the number of recombinations per cubic centimetre would increase with the square of the current, since the force and therefore the velocity of the ions are very little affected by the current.

It also proves that these chemical effects are not due to any internal radiation, such as perhaps the "entladungstrahlen," set up in the positive column by the recombination of ions, for the intensity of such a radiation would probably be proportional to the square† of the current, and certainly could not have a chemical effect dependent only upon the quantity of electricity passed through the gas.

Another result, which is quite independent of any theory of the chemical action, is immediately deducible from Table I. It is this, that the atoms of a molecule of oxygen when dissociated from one another are not charged electrically.

This follows at once from the fact that the chemical output of the

* *E.g.*, to the union of a hydrogen positive ion with a hypothetical negative ion consisting partly of an oxygen atom. It is, however, very probable that a negative ion can only exist in the corpuscular state in a region where Y/p is so large as in Table I.

† See H. A. Wilson, 'Phil. Mag.,' July, 1903, who gives reasons for concluding that the "entladungstrahlen" are due to the recombination of ions.

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positive column is proportional to its length. Now, when the pressure is 0·5 mm., the table shows that $w = 1$. Therefore one molecule of water results from the passage of the atomic charge through 1 cm. of the positive column. Hence, at least one molecule of oxygen is dissociated by the passage of the atomic charge through 2 cm. of the positive column. Now, if the dissociated atoms were charged, one positively, the other negatively, the former would be carried along with the current as a positive ion, while the electron attached to the latter would be torn away from it and add itself to the current. The result would be that an increase of only 2 cm. of the positive column would double the current, and an increase of 18 cm. would multiply the current by ten. In fact, the disturbance produced in the discharge by the chemical action would, if the atoms when dissociated were charged, always be enormous,* whereas it is certain that the chemical effects of the discharge only affect the discharge very slightly, and in a secondary manner by changing the pressure and the composition of the gas.

These considerations prove definitely that the atoms of oxygen, however they come to be dissociated previous to their combining with hydrogen, are during their dissociated state uncharged. Hence their union with hydrogen cannot be attributed to electrostatic forces.

It naturally follows that the forces which bind the atoms of oxygen into molecules of various substances are not electrostatic attractions, and that, if they are of electrical origin, they are electromagnetic, the atoms not being subject to electric force.

Theoretical Consideration of Table I.

It will now be shown that the results recorded in Table I confirm the theory suggested in the writer's previous papers and already stated in this, namely, that the chemical effects of an electric discharge are the result of the collisions of the ions constituting the current with the molecules of the gas, that the molecules, when struck by an ion with sufficient velocity, and under favourable conditions, are broken up into *uncharged* atoms, which are then free to recombine in accordance with dynamical and chemical necessities.

In the preceding paper on this subject it was guardedly assumed that the chemical effects in the positive column are entirely due to the motion of corpuscular negative ions (or electrons). Probably positive ions, by their collision with the gas molecules, are also responsible for similar chemical

* This remark would still be true even if the hypothetical negatively charged atom could move as such in regions where the ratio of electric force to pressure is so great as in these positive columns. It is, however, assumed above, in accordance with well-established results, that negative ions are in the corpuscular state in such regions.

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effects when they move through a region where the ratio of the electric force to the pressure exceeds a certain value, as will be shown later on. But the theory that the chemical effects observed in the positive column are entirely due to the motion of the electrons leads to simple and coherent results which strongly support it.

According to this theory, then, w, which was defined to be the number of molecules of water vapour formed by the transit of the atomic charge through 1 cm. of the positive column, becomes the number of molecules of water vapour formed by the motion of a negative ion through $u_1/(u_1+u_2)$ cm., where u_1, u_2, are the velocities of the negative and positive ions in the positive column. Now u_2/u_1 is quite negligible in regions where the ratio of electric force to pressure is so great as in the positive columns of Table I.* Therefore the theory makes w the number of water-vapour molecules formed by an electron's motions through 1 cm.; and it remains to show that the observed values of w are connected with those of p and Y as the theory requires.

In what follows† it is assumed that owing to their very small mass the electrons are brought practically to rest by their collisions with the gas molecules. It is also assumed (an assumption usually made and easy to justify) that the fields of force here considered impress such a high velocity upon the electrons that the gas molecules may be considered relatively at rest. Now the collision of an electron with a molecule of oxygen cannot have the effect of separating the atoms unless the energy of the electron at collision exceeds the energy of formation of the oxygen molecule, which will be denoted in this paper by η ergs. But besides this condition it is natural to suppose that the electron will not dissociate the molecule unless it collides with a certain minimum velocity.‡ Let V volts represent the potential difference through which the ion must fall to acquire this velocity, then

$$eV/300 > \eta, \qquad (1)$$

e being the charge in electrostatic units of the electron. Hence in a field of force, Y volts per centimetre, the electron must traverse a free path of V/Y cm. or more before colliding with an oxygen molecule if it is to acquire the

* R. T. Lattey, 'Roy. Soc. Proc.,' A, 1910, vol. 84. His numbers make $u_2/u_1 = 0{\cdot}04\ qp$ when this ratio is 0·1. Hence, when Y/p is so large as in Table I, u_2/u_1 is extremely small.

† *Cf.* J. S. Townsend, 'Phil. Mag.,' February, 1901, whose method is here adapted.

‡ The genesis of *uncharged* atoms from the molecules of oxygen by the impact of electrons must not be confused with the genesis of ions by collisions. The former are produced in large numbers when the value of Y/p is so small that only very few ions can be produced. Thus, when $Y/p = 20$, each ion produces on an average 0·94 water molecule per centimetre when p is 1 mm.; for the same force and pressure the number of ions generated in air would be probably 0·01 per cm., and in hydrogen about 0·05.

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necessary velocity of impact to break up the molecule into atoms. Again, let the electron make x collisions with oxygen molecules in moving through 1 cm. in electrolytic gas ($2H_2+O_2$) at a pressure of 1 mm. Then it will make px such collisions in the same gas at p mm. pressure. Now it is well known that of N_1 free paths N_1e^{-n} exceed n times the mean free path l, *i.e.*, $N_1e^{-c/l}$ exceed the distance c. If then $N_1 = px$, $c = V/Y$, $l = \lambda/p$, where λ is the mean free path of the electron in electrolytic gas at 1 mm. pressure, it is clear that the electron will, in moving through 1 cm. of the gas, strike $pxe^{-Vp/Y\lambda}$ molecules of oxygen with velocity great enough to atomise them. But the hit to be effective may have to fulfil other conditions. In that case the number of molecules dissociated will bear a constant ratio to the number struck with adequate velocity. Hence the number of atoms of oxygen dissociated by the motion of the electron through 1 cm. will be $2kpxe^{-Vp/Y\lambda}$, where k, the constant ratio mentioned, is an absolute constant less than or equal to unity.

If each of these atoms of oxygen were to unite with hydrogen to form a molecule of water it would follow at once that

$$w = 2kpxe^{-Vp/Y\lambda}, \tag{2}$$

for, as already explained, w, as originally defined, becomes, from the point of view of the theory, the number of molecules of water vapour formed by the motion of the electron through 1 cm., and if a constant percentage of the liberated oxygen atoms go to form water-vapour molecules, then

$$w = 2\mu pxe^{-Vp/Y\lambda}, \tag{3}$$

where $\mu < k < 1$.

The theory, however, leads presently to the conclusion that an atom of oxygen can combine directly with a hydrogen molecule without the latter's previous dissociation; in other words, if any relative displacement of the atoms in a hydrogen molecule is necessary before the synthesis of water can take place, such a displacement can be effected by the collision of the oxygen atom with the molecule of hydrogen. That being so, a detached atom of oxygen will most probably give rise to a molecule of water vapour, for its chance of meeting a hydrogen molecule is obviously much greater than its chance of meeting another atom of oxygen, and the probability of its uniting with oxygen is proved to be small by the small amount of ozone that is generated by the discharge. The conclusion to be drawn is that μ is nearly the same as k.

If w/p, Y/p are denoted by w_1, Y_1, equation (3) becomes

$$w_1 = ce^{-V/\lambda Y_1}, \tag{4}$$

where

$$c = 2\mu x, \ (\mu < 1), \tag{5}$$

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so that c is less than twice the number of collisions which an electron makes with oxygen molecules in moving through 1 cm. in electrolytic gas at 1 mm. pressure.

Now it is easy to deduce approximate values for λ and x from the experimental results of Prof. J. S. Townsend and Mr. H. E. Hurst, according to which an electron moving rapidly under electric force makes* 15·2 collisions per centimetre in air at 1 mm. pressure and 13·6 collisions in nitrogen at the same pressure. Hence in nitrogen at 0·79 mm. pressure an electron would make $13{\cdot}6 \times 0{\cdot}79$ collisions per centimetre $= 10{\cdot}75$, and therefore $15{\cdot}2 - 10{\cdot}75$ or 4·45 collisions per centimetre with the molecules of oxygen if moving in oxygen at 0·21 mm., and therefore would make 7·06 collisions in oxygen at 0·333 mm. Hence an electron would make 7·06 collisions with oxygen molecules in passing through 1 cm. of electrolytic gas at 1 mm. pressure. Hence

$$x = 7{\cdot}06. \tag{6}$$

It is, however, important to point out that the value of x thus deduced may have a very large percentage error. For instance, if the numbers 15·2, 10·75, involve moderate experimental errors of 3 or 4 per cent., their difference 4·45 *may* involve an error of more than 20 per cent. This would be unlucky, but an error of 10 per cent. is quite probable.

Again the electron makes† 5·5 collisions per centimetre in hydrogen at 1 mm. pressure, so that in electrolytic gas it makes $5{\cdot}5 \times \frac{2}{3} = 3{\cdot}67$ collisions with hydrogen molecules in moving rapidly through 1 cm.

Therefore

$$\lambda^{-1} = 7{\cdot}06 + 3{\cdot}67 = 10{\cdot}7. \tag{7}$$

This value of λ^{-1} is infected with the large errors which may lie in the value 7·06 obtained for x. But fortunately a more exact knowledge of x and λ is not necessary in order to establish the complete agreement between the experimental results recorded in this paper and the theory suggested to explain them.

Agreement of the Theory with the Experimental Results.

Equation (4), $w_1 = ce^{-V/\lambda X_1}$, agrees with the form of the curve drawn in fig. 4 if

$$V/\lambda = 42{\cdot}7, \tag{8}$$

and

$$c = 7{\cdot}9, \tag{9}$$

thus satisfying the condition of equation (5) that $c < 2x$, *i.e.* $< 14{\cdot}1$. This agreement is shown in Table II.

* J. S. E. Townsend, 'Phil. Mag.' [5], 1903, pp. 389—398; H. E. Hurst, 'Phil. Mag.,' April, 1906.

† J. S. Townsend, *ibid.*

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Table II.

Y_1	17	20	21·3	25	30	40	50
$7{\cdot}9\,e^{-42{\cdot}7/Y_1}$	0·64	0·94	1·07	1·43	1·91	2·71	3·38
Ordinate of curve	0·64	0·92	1·08	1·44	1·96	2·8	3·36

Thus the curve defined by the equation

$$w_1 = 7{\cdot}9\,e^{-42{\cdot}7/Y_1}, \qquad (10)$$

the form of which is given by the theory, is practically the same as that determined by the points plotted in fig. 4, *i.e.* by the experimental results of Table I.

In connection with this agreement of the theoretical curve with the experimental, it is important to point out that small errors in Y_1 when Y_1 is considerably less than 42·7 may throw the corresponding point seriously off the curve, even if the corresponding value of w_1 is correctly determined, for equation (10) gives $\delta w_1/w_1 = (42{\cdot}7/Y_1)\,\delta Y_1/Y_1$. This fact will explain the relatively large divergence from the curve of some of the points of smaller abscissæ in fig. 4. It was on account of these divergencies that so many points in this region of the curve were determined in order to ascertain the true position of the curve.

It may also be noticed that the curve (10) has only one inflexion, where $Y_1 = 21{\cdot}3$, and that the curvature is convex to the left and concave to the right of it. The curve in fig. 4 has been drawn to satisfy these conditions, and it is, within the limits of error, the mean locus of the points plotted; but the curvature is too slight, and the exact position of the point to the extreme left too uncertain, for the reasons just given, to attach much weight to these considerations.

The Relation Between w, p, and Y Probably Absolute.

It follows from the preceding discussion that the theory is in complete agreement with experiment as far as it has has been found possible to verify it. The obstacles to a more complete verification are inherent in the method and consist of the limited range of variation of w and Y, and the fact that it is not possible to vary Y, at least to any great extent, independently of p. On the other hand, the approximate relation (10) between w/p and Y/p is well supported by the few similar results* that were deduced by the writer from

* 'Phil. Mag.,' March, 1907. The value of Y corresponding to $p = 2{\cdot}1$ was determined in this paper by a graphic method from the curve, p. 301, corresponding to the pressure 2·1 mm., as 40; but a revaluation by the same method shows that 37 would be nearer the mark. If this correction is made, the four pairs of values of Y/p, w/p, corresponding to the pressures 4·5, 2·1, 1·05, 0·65, satisfy equation (10) well enough.

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some similar experiments which were made with a different apparatus and much greater currents, the forces in the positive columns being appreciably different at the same pressure. Thus the observed values of w are found to respond to any change that has arisen in Y. These considerations lead to the conclusion that the approximate equation (10), viz., $w/p = 7{\cdot}9e^{-42{\cdot}7/(Y/p)}$ between w, p, Y is probably an absolute relation; namely, it is a relation independent of the apparatus and not confined to positive columns but existing between the chemical effects of an electron's motion, through electrolytic gas ($2H_2+O_2$) and in any field of electrostatic force Y, and Y and p. It is true that special conditions prevail in the positive column where these effects have been observed, and that a certain amount of recombination may be going on, so as to terminate the course of a percentage of the electrons that traverse it. That percentage is, however, probably* negligible; and in any case, ions are produced at exactly the same rate as they disappear, since everything is quite steady, so that the mean chemical effects attending the passage of the atomic charge through 1 cm. of the positive column must be the same as though that charge was carried by the same electron. Thus there is no reason to suppose that the relation (10) between w, p, Y, in the positive column would not equally exist anywhere else where there may be an electrostatic force Y.

Deductions from the Theoretical Equation.

The equation $w_1 = 7{\cdot}9e^{-42{\cdot}7/Y_1}$ leads to several results which will now be deduced.

(1) *Approximation to the Energy of Formation of an Oxygen Molecule.*—Since $V/\lambda = 42{\cdot}7$ and $1/\lambda = 10{\cdot}7$ by equations (8) and (7), therefore $V = 4$ volts.† That is, an electron must fall freely through at least 4 volts to acquire sufficient velocity to dissociate by impact an oxygen molecule into atoms. Hence by the inequality (1) η, the energy of formation of an oxygen molecule, is less than $(4e/300 =)\ 6{\cdot}1 \times 10^{-12}$ ergs, since the charge e of an electron seems‡ to be nearly $4{\cdot}6 \times 10^{-10}$ electrostatic units; and since the present theory assumes that the electron is practically stopped by its collisions, so that nearly all its energy is imparted to the molecule struck, the limit, $6{\cdot}1 \times 10^{-12}$ ergs, should be fairly near to the actual value of η. This estimate is independent of the quantity of water

* Because of (1) the low pressures, (2) the very high velocity of the stream of electrons for such large values of Y/p, as recently proved by Mr. R. T. Lattey (*loc. cit*), (3) the very small current density of that stream, which is necessitated by (2).

† The limit 6·4 volts was previously deduced by the writer by rather different reasoning, 'Phil. Mag.,' March, 1907.

‡ Rutherford, Address to British Association, 1909; R. T. Lattey, 'Phil. Mag.,' July, 1909.

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vapour present (which it might perhaps be thought would lower the energy of formation of a molecule), for the amount of water vapour present depends on the strength of the current, and equation (10), from which the estimate is deduced, is independent of the current. But it is, of course, subject to any correction necessitated by possible errors in the value of λ.

The limit just found for η receives support from other researches. Berthelot* found by experiments on the oxidation of arsenious acid that when two gramme-molecules (96 grammes) of ozone passed into oxygen 61400 calories of heat were liberated. From this datum a value for η, which is probably a lower limit, can be obtained. Let it be assumed provisionally that when two molecules of ozone pass into three of oxygen the energy set free is simply due to the formation of one molecule of oxygen. Then, when 1 c.c. of ozone is transformed into oxygen, $\frac{1}{2}N\eta$ ergs of energy will be liberated, where N is, as usual, the number of molecules of a gas in 1 c.c. at 760 mm. pressure and 15° centigrade. But Berthelot's numbers give 1·31 calories as the heat of transforming 1 c.c. of ozone at 760 mm. and 15° C. into oxygen.

Therefore $\frac{1}{2}N\eta = 1{\cdot}31 \times 4{\cdot}2 \times 10^7$ ergs and $Ne = 1{\cdot}22 \times 10^{10}$.

Hence, since $e = 4{\cdot}6 \times 10^{-10}$, $\eta = 4{\cdot}1 \times 10^{-12}$ q.p.

This value has been obtained by neglecting the work required to detach one atom from the ozone molecule, and by assuming that the potential energy of the remaining pair of atoms is unaltered. If, however, a substantial amount of work is needed to detach the atom, the number obtained for η is too small, unless the rearrangement of the remaining atoms liberates enough energy to balance that lost in detaching the one atom from the molecule. Probably then η exceeds $4{\cdot}1 \times 10^{-12}$ ergs.

Mulder and Van der Meulen,† revising Berthelot's work, obtained rather larger values which would lead to $4{\cdot}4 \times 10^{-12}$ ergs: and Van der Meulen, by direct determination of the heat of decomposition of ozone, obtained still higher values for the same quantity, which would lead to $4{\cdot}9 \times 10^{-12}$ ergs, instead of the $4{\cdot}1 \times 10^{-12}$ ergs deduced above, as probably a lower limit for η. If the value $4{\cdot}5 \times 10^{-12}$ ergs is adopted as a mean and taken as a lower limit for η, it follows that the superior limit $6{\cdot}1 \times 10^{-12}$ ergs found above for η is fairly close to its true value as the theory suggests.

(2) *Hydrogen must Combine Directly with Atomic Oxygen.*—The equation $w_1 = 7{\cdot}9\, e^{-42{\cdot}7/Y_1}$, involves the consequence that if Y_1 is great enough, w_1 approaches 7·9 as its limiting valve. That is, an electron might, in

* 'Thermochimie,' 1897, vol. 2, p. 44. This was a revised estimate of the original value given, 'Ann. Chim. Phys.' [5], vol. 10, p. 164.

† 'Rec. Trav. Chim. Pays Bas,' vol. 1, pp. 65 and 73.

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moving through 1 cm. of electrolytic gas at 1 mm. pressure under a large force, cause the formation of 7·9 molecules of water. But an electron has been shown (see equation (7)) to make only 3·7 collisions with the hydrogen molecules in so moving, and therefore could not produce more than 7·4 atoms of hydrogen, which, if it were necessary for the synthesis of water to bring the hydrogen to the nascent or atomic state, would not be sufficient to produce more than 3·7 molecules of water vapour.

On the other hand (see equation (6)) an electron in moving through 1 cm. of electrolytic gas at 1 mm. pressure makes 7·06 collisions with oxygen molecules, so that if only 4 out of these collisions dissociated the molecules into atoms, there would still be enough detached oxygen atoms for the production of the 7·9 molecules of water.

It follows from these considerations that an atom of oxygen is capable of uniting directly with a *molecule* of hydrogen. In other words, if the atoms in a hydrogen molecule need to be relatively displaced previous to the formation of water, such a displacement can be effected by the collision of the free atom of oxygen.

This conclusion is supported by the form of equation (10), which requires that only one of the gases need be brought to the active state. For if the hydrogen had also to be atomised by ionic impact, the amount of water vapour would be proportional to the product of $2pxe^{-Vp/Y\lambda}$ and a similar term applicable to hydrogen (see equation (2)). Hence would

$$w/p^2 = ae^{-bp/Y},$$

(a, b, constants), and w/p^2 would be a function of Y/p: the latter result is inconsistent with one or two observations in this and the last paper, and the former does not appear to be reconcilable with the rest.

(3) *Energy of Formation of a Molecule of Water Vapour.*—From the two previous conclusions (1) and (2) it is possible to form an estimate of the energy of formation of a molecule of water vapour. For, as is well known, 1 grm. of hydrogen, uniting with oxygen to produce water vapour at laboratory temperature, liberates 29,000 calories of heat, that is $1{\cdot}22 \times 10^{12}$ ergs, and consists of $1{\cdot}44 \times 10^{14}/e$ molecules, e being as before the atomic charge, e.s.u. Therefore the formation of each molecule of water vapour sets free $3{\cdot}9 \times 10^{-12}$ ergs. But when two molecules of water vapour are formed, one molecule of oxygen must be separated into atoms, costing between 4×10^{-12} and 6×10^{-12} ergs by (1). Hence the energy of formation of a molecule of water must lie between $5{\cdot}9 \times 10^{-12}$ and $6{\cdot}9 \times 10^{-12}$ ergs, being nearly $6{\cdot}4 \times 10^{-12}$ ergs. This estimate would have to be increased if it were necessary to suppose that a comparable amount of energy had to be

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spent in dissociating into atoms a molecule of hydrogen. But by (2) this is not *necessarily* the case. According to this result the oxygen molecule is nearly as stable as one of water vapour, a result which accounts for the great stability of electrolytic gas at ordinary temperatures.

(4) *The Proportion of Effective Collisions.*—It was pointed out in the discussion of (2) that an electron would cause the formation of 7·9 molecules of water in moving through 1 cm. of electrolytic gas at 1 mm. pressure if the electric force were great enough. But in so moving it collides x times with oxygen molecules, and x has been found equal to 7·06 (equation (6) above). It follows that the impinging electron, no matter how great its velocity, can only dissociate into atoms an oxygen molecule at, roughly,* every other impact. This result admits of an obvious explanation if the dissociation of the molecule is attributed to the mechanical effects of the collision. For the colliding electron would not separate the two atoms of the molecule unless the impulse due to the collision carried the atom struck away from its companion atom. But, however the two atoms may move together as one dynamical system, a blow concentrated at a point, such as that due to an impinging electron, and applied at random to the moving molecule, would drive the atom that received the blow towards the other atom just about as often, probably, as away from it. Hence only about half the number of collisions that an electron makes with oxygen molecules, with sufficient velocity to dissociate them, can succeed in doing so.

Effects of Temperature upon Chemical Activity.

A few experiments were made to ascertain the effect of temperature upon the chemical activity of the discharge. The discharge tube was surrounded by a vessel containing a freezing mixture, and the value of W determined at pressures of about 0·7 mm. The result showed that the total activity was lowered by lowering the temperature, but by only a percentage not exceeding the percentage diminution in the absolute temperature.

General Discussion.

The theory developed above, which attributes the chemical action in the positive column to the action of electrons alone, is sufficient to explain fully all the complicated effects therein observed in electrolytic gas. According to

* Or, perhaps, accurately ; since, as shown in connection with equation (6), the value 7·06 of x may involve a large percentage error. [Since this note was written, Prof. Townsend's 'Ionisation of Gases by Collision' has come to hand containing (p. 24, *f*) revised numbers. These would make $x = 7·6$, so that "roughly" may perhaps be omitted. It should be added that the value of $1/\lambda$ of equation (7) is scarcely affected, the new numbers giving 10·9 instead of 10·7.]

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it, an electron is capable by collision of breaking up an oxygen molecule into uncharged atoms, just as Prof. Townsend has shown it can break up a molecule into ions. It follows from the numerical results that the same collision might at once both atomise and ionise a molecule; another collision might have either of these two effects without the other, according to the velocity and other circumstances of the impact. For the work* required to ionise a molecule of a gas, except in peculiarly favourable circumstances of ionic impact, is much greater than the work needed to dissociate a molecule of oxygen into atoms; and, on the other hand, ionisation may occur at every impact, if the velocity is great enough, but not dissociation into atoms.

Again, since positive† ions have also the power of ionising molecules by collision, it is highly probable that they can perform the task, lighter in respect of work to be done, of breaking up molecules of oxygen into atoms, if they are moving in a strong enough field of force. Thus it is possible that the great chemical activity in a discharge across the cathode fall may be the work of the positive ions, though there is no direct evidence of this.

With regard to other reactions produced by an electric discharge, it is natural to assume that the part played by it in promoting chemical action is the same.

The collisions of the ions, probably both kinds, with the molecules of gas bring the gas into the active state, either by dissociating or displacing the atoms, so that it can form new combinations. It follows that different chemical products might be formed in the same gaseous mixture by the motion of ions under different fields of force.

This theory does not dispense with the postulate of chemical forces acting selectively, but only explains how the discharge prepares the way for their action. On the contrary, it was pointed out above that the experimental results, quite independently of theory, lead certainly to the conclusion that the atoms of oxygen when separated are not charged electrically, so that it is necessary to postulate some other force that binds them into a molecule.

The connection between w, p, and Y, expressed in equation (4), owes its form partly to the fact involved in the theory that only one of the constituents of electrolytic gas (viz., oxygen) has to be brought to the active state in order to produce the reaction. In fact the quantity m_1 of one of the components of a gaseous mixture M that can be brought to any active

* J. S. Townsend, 'Phil. Mag.' [5], 1903.

† J. S. Townsend, 'Phil. Mag.,' November, 1903.

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state A by the motion through 1 cm. of an ion (of either kind) under an electric force X must satisfy Townsend's functional equation*

$$m_1/p = f(X/p), \tag{11}$$

since m_1 is obviously proportional to the number of collisions which the ion makes per centimetre of a certain type, namely, the type of collision which owing to the velocity and other circumstances of impact can bring the molecule struck to the state A. Equation (4) is of the functional form (11), as must evidently be the case, since the quantity of water w, formed per centimetre of the electron's motion, is proportional simply to the amount of oxygen brought to the active state per centimetre of that motion.

If, however, the reaction between two constituents of the gaseous mixture M set up in a gas by a current can only take place if both constituents are brought to an active state different from their ordinary condition, then, by the law of mass action, the amount m of the chemical product formed per centimetre of the ion's motion will be proportional to the product of m_1 and m_2, where m_2 is the quantity of the other reacting substance brought to the active state per centimetre of the ion's motion. And since

$$m_2/p = \phi(X/p),$$

therefore

$$m/p^2 = \psi(X/p).$$

Similarly, if three substances combine under the same conditions, the mass of the product formed per centimetre of the ion's motion would satisfy $m/p^3 = \psi(X/p)$, and so on.

The total amount of a chemical product formed per second by a gaseous electric current of either sign is obtained by a volume integration when ν, the chemical activity at any point P (mass of the product resulting from the flow of unit quantity of electricity past the point per centimetre of that flow) is known in terms of the pressure p and the electric force X at P. For if ρ is the density of the ionic stream past P and u its velocity, the quantity of electricity that passes a small area δA perpendicular to the direction of the current is $e\rho u\,\delta A$ per second; and this after flowing a distance δs will give rise to the mass $\nu e\rho u\,\delta A\,\delta s$ of the product. Hence the whole product per second produced by the current will be

$$\int \nu e\rho u d\tau,$$

where $d\tau$ is the element of volume at the point P. In the general case where the current consists of two streams of positive and negative ions, the total chemical product per second of the current will consist of the sum of two such

* J. S. Townsend, 'Phil. Mag.,' February, 1901.

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volume integrations. If ν applies to the effects of the motion of a single ion, e must of course be replaced by unity.

In the case of such currents as can be made (*e.g.* by means of the Röntgen rays, ultra-violet light, radium, &c.) to pass between two electrodes without disturbing the electrostatic field, ρ is so small that the mass of the chemical product would not be detectable. It is only in the case of very much larger currents, such as those maintained through a gas by a battery, or those obtained by connecting the electrodes to the secondary terminals of a Ruhmkorff coil, as in the case of the silent discharge, that a sufficient number of effective collisions are made by the ions traversing the gas to produce a measurable effect.

Summary of Principal Conclusions.

(1) When a steady discharge passes through electrolytic gas at pressure p mm., the number of molecules of water vapour formed by the passage of the atomic charge through 1 cm. of the positive column, where the electric force is Y, is approximately $7{\cdot}9pe^{-42{\cdot}7p/Y}$. This number, which is independent of the current, appears to be absolute (*i.e.* independent of the apparatus and not confined to positive columns) and to depend only upon the field of force.

(2) The atoms of oxygen, when separated, are not charged electrically. This is proved by experiments independently of theory. Hence the atom of oxygen is not bound in a molecule of water vapour by electrostatic force.

(3) The chemical effects, within the positive column, are due to the collisions of the (corpuscular) negative ions with the oxygen molecules, which are dissociated into atoms, under certain conditions, by those collisions, and so enabled to combine with hydrogen.

(4) The energy of formation of an oxygen molecule is less than $6{\cdot}1 \times 10^{-12}$ ergs, and is nearly equal to $5{\cdot}3 \times 10^{-12}$ ergs.

(5) Water vapour is produced by the collision of an atom of oxygen with a *molecule* of hydrogen.

(6) The energy of formation of a molecule of water vapour is nearly $6{\cdot}4 \times 10^{-12}$ ergs.

(7) Only half the collisions that an electron makes with a molecule of oxygen, with sufficient velocity to dissociate it, succeed in doing so.

In conclusion, the writer wishes to express his many obligations to the work of Prof. Townsend, whose researches on the ionisation of gases by collision have made possible the present research (which was carried out in his laboratory) and to thank him for his suggestions. He also wishes to express his obligations to Mr. A. F. Walden, Fellow of New College, for some valuable information.

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Atmospheric Electricity over the Ocean.

By G. C. Simpson, D.Sc., and C. S. Wright, B.A.

(Communicated by Arthur Schuster, F.R.S. Received January 20,—Read January 26, 1911.)

Although the different phenomena of atmospheric electricity have been thoroughly investigated over land, very little work has yet been done over the ocean, and on the few occasions on which experiments have been made, the observations have been too few to give conclusive results. It was thought that the long voyage from England to New Zealand of Captain Scott's Antarctic ship "Terra Nova" would furnish an excellent opportunity for continuing these investigations. The plan of the work to be undertaken was:—

(1) To investigate the electrical potential-gradient existing over the ocean.

(2) To investigate the quantity of the radioactive products in the air.

(3) To measure the number of free ions over the ocean.

(4) To investigate the ionisation of the air in a closed vessel, with the object of determining the presence or absence of a penetrating radiation over the sea.

One of the chief difficulties which has hindered the work of previous investigators has been the want of a suitable electroscope for use on the sea, the only instrument which had been available being the leaf electroscope in one or other of its numerous forms. It is obvious that this instrument could not be used with accuracy on a ship rolling to an appreciable degree. There has, however, recently been put upon the market an electroscope designed by Prof. P. T. Wulf, of Holland,* which does not depend upon gravity for equilibrating the electrical force, but upon the tension of a small bow of quartz fibre. This instrument, which is excellently made by Günther and Tegetmeyer, of Brunswick, has been used in all our work, and has proved itself capable of giving a high degree of accuracy, even when the ship was rolling as much as 25° from the vertical.

(1) *Potential-gradient.*

As far as we have been able to discover, the only measurements of the potential-gradient made over the sea are those of Exner, who observed during a voyage from Aden to Bombay in 1888.† Exner's results are valuable, but they do not settle the three important questions:—

(1) Is the potential-gradient over the centres of the great oceans of the same sign as over the land?

* Wulf, 'Phys. Zeit.,' 1907, vol. 8, pp. 246, 527.

† Exner, 'Wien. Ber.,' 1899, vol. 108, p. 371.

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(2) Is it of approximately the same magnitude?

(3) Is the daily range over the ocean similar to that over the land?

It is towards the solution of these problems that our work has been directed.

Our methods were in the main similar to those used on land, but instead of a water-dropper or a flame, we used a radioactive substance for bringing the collector-rod to the potential of the air at its end. Objections have been raised against the use of radium itself for this purpose, as the β- and γ-rays ionise the air to a considerable distance from the radium, so that not only are the conditions under investigation affected by the presence of the radium, but it is impossible to fix with sufficient accuracy the point in the atmosphere to which the potential measured by the instrument refers.

On talking over with Profs. Elster and Geitel the question of the best collector to be used in the Antarctic, they suggested ionium, because this element does not appreciably decay with time and gives out only α-rays, the ionising power of which is limited to a few millimetres. Prof. Giesel generously placed a comparatively large amount of this rare substance at our disposal, and Profs. Elster and Geitel very kindly experimented to determine the best method of applying it to the ends of our collector rods. The collector as used consisted of a short copper rod coated with ionium, attached to a thin wooden rod 110 cm. long, cemented by means of sulphur at its lower end into a brass tube. The latter was then fastened by means of grips to a retort stand, the sulphur cement efficiently insulating the rod from the earth-connected stand. A wire connected the collector to a Wulf electroscope.

The Sign of the Potential-gradient.—During the whole voyage, observations were made every few days to determine the sign of the potential-gradient, and it was found to be, without exception, positive on fine days.

The Daily Range of the Potential-gradient.—In order to obtain the form of the curve representing the daily range of the potential-gradient, it is only necessary to fix the collector in some position, the surroundings of which do not change, and then to take observations during periods of fine weather. This, however, was found to be impossible on the "Terra Nova," for there was absolutely no spot on the ship which was not dominated by yards, sails, and ropes, the positions of which were constantly being changed. The only thing to be done was to take every opportunity of a spell of settled weather to make observations, when there was a probability of the sails remaining in one position for several hours. On each occasion the most suitable position on the ship in which to set up the collector had to be chosen; in some cases this was in the bow of the ship, and in others at the stern. Thus no two series of

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measurements could be joined up, for even when the same position was used a second time, the yards were probably trimmed differently at each observation. As a set of observations was of little use unless it extended over a period of approximately 24 hours, during which the sails and yards were not moved, a large amount of work was wasted, for observations were started on several occasions which had to be abandoned owing to a change in the position of the sails, or to a change in the weather conditions which disturbed the normal potential-gradient.

The method of making the observations was as follows:—The position for the collector being chosen and the apparatus set up, the electroscope was read at the end of each minute. It was deemed necessary to make these frequent readings in order to get a mean which would be independent of the rapid changes of the potential-gradient, and would cut out errors due to the changing position of the collector relative to the sea surface caused by the roll of the ship.

Table I gives the result of the few series which were sufficiently extended to be useful for our purpose. With the exception of Series IV, V, and VI, the numbers are on an arbitrary scale, and, as stated above, those of one series are not directly comparable with those of another. The mean value for an hour is the mean of the 60 readings extending from half an hour before to half an hour after the hour.

The numbers are plotted in the respective curves of fig. 1.

Series I.—The observations commenced at 17 h. 30 m. (mid-day written 12 h.) on July 14, when the ship was in lat. 2° N. and long. 21° 36′ W., and extended to 10 h. 30 m. on July 16, when the position of the ship was 0° 58′ S. and 21° 17′ W. Thus the whole series was obtained within nearly 2° of the Equator. The weather was fine during the whole period, with cloud amounts varying from 0 to 6. The observations had to be stopped owing to the setting of the sails.

Series II extended from 15 h. 30 m. on July 21 to 13 h. 30 m. on July 22, the position of the ship being 11° 15′ S. and 26° 2′ W. at the commencement, and 12° 34′ S., 27° 5′ W. at the end. The weather was not at all satisfactory during this series of observations. When the observations commenced the sky was clear to within 20° of the horizon, but in the east there was a bank of fairly heavy stratus clouds. This bank steadily rose and became thicker, and at 18 h. 15 m. clouds from it had reached the zenith. At 19 h. 30 m. the sky was quite overcast with cumulo-stratus clouds, and at 20 h. 22 m. a few drops of rain fell. From this time until 22 h. 36 m. there were rain squalls on the horizon, and every now and then a few drops of rain would fall on the ship. The clouds commenced to clear at 22 h. 40 m.,

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Table I.

	Series I.			Series II.		Series III.	Series IV.			Series V.		Series VI.
	Arbitrary scale.			Arbitrary scale.		Arbitrary scale.	Volts/metre.			Volts/metre.		Volts/metre.
	July 14.	July 15.	July 16.	July 21.	July 22.	July 25.	Aug. 3.	Aug. 4.	Aug. 5.	Sept. 24.	Sept. 25.	Sept. 26.
Midnight		304	274		183			116	124		130	
1		305	273		206			108	128		138	
2		312	300		201			96	108		125	
3		298	342		202			100	100		136	
4		280	392		211			108			107	
5		281	395		222			108			109	
6		289*	446*		224*			100*			—*	
7		300	397		217			96			97	
8		273	367		216			96			101	
9		225	383		213	243		76			99	
10		232	337		215	236		96				79
11		215			218	217		104				77
Midday		249			216	209	84	96				81
13		251			203	218	96	84				80
14		—				218	104	92				76
15		305				208	100	92		100		85
16		332		247		238	108	88		93		86
17		387		263		260	116	124		88		
18	397†	382†		253†			120†	156†		94†		
19	400	381		256			124	148		91		
20	378	361		231			136	164		103		
21	389	335		245			140	144		106		
22	328	314		232			136	124		110		
23	312	286		208			136	108		123		

* Sun rose during this hour.

† Sun set during this hour.

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and by 1 h. they had practically all disappeared; after this the cloud amount remained below 4, until the observations were stopped.

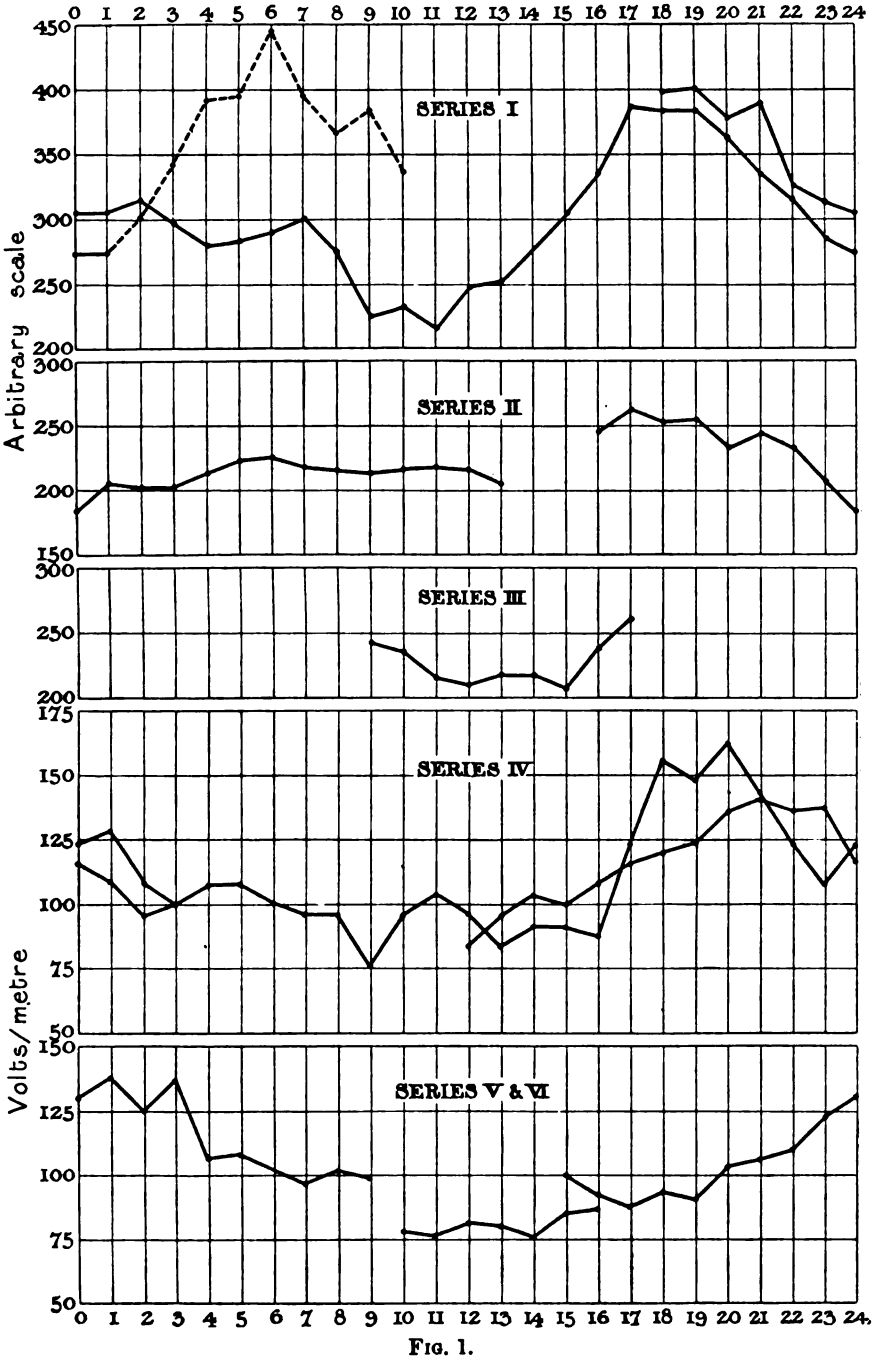

FIG. 1.

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Series III was obtained on July 25, when the position of the ship was 19° 27′ S. and 29° 24′ W., within a few miles of the island of South Trinidad. The weather during this period was quite fine, with very little cloud. It is much to be regretted that this series could not have been continued, but the sails were furled soon after 17 h., and the observations had to cease.

Series IV was the most successful set of observations obtained during the whole voyage. It commenced at 11 h. 30 m. on August 3 in 30° 18′ S. and 19° 28′ W., and continued until 3 h. 30 m. on August 5 in 31° 30′ S. and 15° 0′ W. For nearly 26 h. from the commencement the sky was practically clear of clouds, but from 13 h. on the 4th the weather was very unsettled, heavy squalls passing near the ship. At 16 h. a little rain fell; the clouds then cleared somewhat until 18 h. 30 m., after which they became thick again, and between 21 h. and 23 h. there was more slight rain. From this time until the observations were stopped at 3 h. 30 m. on the 5th the weather was unsettled, and the wind rose rapidly.

After leaving Cape Town it was not expected that there would be any opportunities of making further observations of the potential-gradient, as the weather generally met with between the Cape and Australia is very rough. The weather experienced by the "Terra Nova" was, however, exceptional, and we had several days when the sea was almost smooth. On these days there was a great deal of cloud and a continual succession of small squalls, each bringing a little rain. Several attempts were made to get observations of the potential-gradient, but they were not very successful. Series V and VI were the two best.

Series V was obtained between 14 h. 30 m. on September 24 and 9 h. 30 m. on the 25th, the position of the ship being 39° 21′ S. and 84° 58′ E. at the commencement and 39° 49′ S. and 87° 19′ E. at the end. Until 23 h. on the 24th the sky was nearly clear, but from then on the weather was unsettled, and before midnight several light showers were experienced. After midnight the sky underwent very rapid changes of cloud amount, sometimes being quite overcast and a few minutes afterwards nearly clear. Finally it started to rain, and the observations had to be abandoned at 9 h. 30 m.

Series VI was obtained on September 26, the position of the ship being 40° 26′ S. and 91° 24′ E. During the observations the sky was almost cloudless, but soon after 16 h. a heavy squall came up. The weather did not clear again sufficiently to allow of the observations being continued.

The most uniform feature of the curves in fig. 1 is the rise in the potential-gradient during the afternoon and early evening. Every curve shows this,

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but the time at which the maximum occurs is somewhat different in each case, varying from 17 h. in Curve 1 to 1 h. in Curve 6. The latter curve, however, was no doubt largely influenced by the bad weather, and the time of maximum delayed by the showers which occurred before midnight. It appears, however, to be quite safe to conclude that the curves have their chief maximum during the evening or the early hours of the night. From this maximum each curve falls away, and there is a general tendency to fall until mid-day. All the curves reach their minimum through greater or less irregularities, which are no doubt caused by transient weather changes.*

Although these few curves leave much to be desired, they appear to show that the potential-gradient over the ocean within 40° of the Equator has its chief maximum in the evening and its chief minimum soon after mid-day.

In order to estimate the importance of these conclusions a few words must be added on the potential-gradient over the land. In high latitudes (*e.g.*, Cape Thordsen in Spitzbergen and Karasjok in Lapland) the potential-gradient has a simple daily range with a well-marked minimum at about 4 h. in the morning and a maximum between 18 h. and 21 h. in the evening. In temperate regions (*e.g.*, Kew, Paris, and Potsdam) the curve is similar, but with a second minimum superposed at about 14 h. This afternoon minimum is everywhere more pronounced in the summer than in the winter. In the tropics (*e.g.*, Batavia) the second minimum increases to such an extent that it becomes predominant, and at Batavia the 4 h. minimum is almost insignificant in comparison with the deep one at 13 h. It is generally held that the simple curve as exhibited in the winter and in high latitudes represents the fundamental march of the potential-gradient, and that the afternoon minimum is the result of the disturbance caused by the large amounts of dust which are raised by ascending currents where solar energy is intense; hence the predominance of this minimum in the summer and at low latitudes. This explanation is also supported by the fact that the potential-gradient on high mountains (*e.g.*, Sonnblick and Dodabetta) and at the top of the Eiffel Tower, which are supposed to be above the main mass of dust raised from the ground, has the simple daily curve.

It was therefore to be expected that over the ocean the simple daily range with its single minimum at 4 h. and its maximum in the early evening

* The large rise in the potential gradient shown after 1 A.M. at the end of Curve 1 was accompanied by the sudden formation at sunrise of fairly heavy clouds in a nearly clear sky; these cleared away within an hour of their formation; this part of the curve has therefore been dotted in fig. 1.

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would be found. The curves in fig. 1 show, however, that this is not the case, for there is hardly any evidence of a minimum at 4 h. and a most marked one at about mid-day. From these results it would appear that the second minimum is not entirely due to raised dust, but is the result of some more fundamental cause.

It is possible that the daily range of the potential-gradient is dependent on latitude. Our observations on the sea were all obtained within about 40° of the Equator, and they show in common with land observations within the same latitudes a predominant minimum at about mid-day; in high latitudes land observations show the predominant minimum at 4 h., while between these two extremes we have the two minima occurring together, but with varying relative intensities. May not therefore the afternoon minimum be of equal importance with the morning one, instead of being a disturbance caused by dust-charged convection currents? If this is found to be the case, then the 4 h. minimum may be considered the polar minimum and the mid-day one the equatorial minimum.

Non-periodic Changes.—With regard to minor fluctuations of the potential-gradient it may be remarked that just as is the case over the land the potential over the sea undergoes changes from minute to minute. As an example, the following readings taken at minute intervals from 14 h. to 14 h. 15 m. on August 3, have been extracted haphazard from our note-book; at the time the sky was cloudless except for a few small cumulus clouds on the horizon:—32, 30, 40, 47, 43, 57, 50, 32, 30, 31, 35, 47, 30, 55, 36, 35.

The effect of rain was found to be the same on the sea as on the land. As the rain approached the potential-gradient generally decreased, and during one period of steady rain, negative potential-gradient was noted. When, however, the rain was associated with a squall the potential-gradient took on large values, which changed rapidly from one sign to the other just as it does during a thunderstorm on land.

Absolute Value of the Potential-Gradient.—On our arrival at Melbourne (Australia) we found it possible to obtain the reduction factor for converting the relative observations of three of our series into absolute units. Within 1000 yards of the ship at anchor was a level beach, over which the equi-potential surfaces were practically horizontal. Here one of us set up the apparatus for making the absolute determinations. Two rods, with insulators on their ends, were erected 18 metres apart. In one set of readings the rods were 46 cm. high, and in another set 79 cm. Thus the field midway between them was not disturbed, for they were too far apart. A fine wire was stretched from insulator to insulator as tightly as possible, so that it was

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practically horizontal. To the middle of the wire an ionium collector was attached. This brought the wire to the potential in its neighbourhood, and as the wire was horizontal it lay in an equipotential surface, and so had no tendency to disturb the field. This method appears to be better than any other yet used for determining the absolute potential-gradient, since the field in the neighbourhood of the collector is as undisturbed as it is possible to obtain it.

While observations were being taken on shore, measurements were made on the ship with the conditions of yards and ropes as similar as possible to those during three of our sets of observations at sea. From the simultaneous observations the reduction factors were found, and have been applied to the figures in Columns 4, 5, and 6 of Table I. From these columns we see that the mean hourly potential-gradient on August 3 and 4 varied from 76 volt/metre to 164 volt/metre; on September 24 it varied from 87 to 138 volt/metre, while on September 24, for a few hours about mid-day, it varied around 80 volt/metre. These numbers cannot claim to have any great degree of accuracy, but, taking into account all the circumstances, it is probable that the errors are less than 25 per cent. Thus we obtain the important result that the potential-gradient over the South Atlantic Ocean and the South Indian Ocean, far away from land, is very similar in amount to that over the land.

(2) *Radioactivity.*

When Elster and Geitel discovered the presence of radioactive emanation in the atmosphere, they suggested that it owed its origin to the radium of the soil and rocks. As radium is constantly giving off emanation the interstices of the soil must be full of emanation, and Elster and Geitel experimentally demonstrated its presence. This emanation diffuses out of the earth, adding a short-lived gas to the atmosphere. Owing to the minute quantities of radium in sea-water, it seemed probable that the air over the ocean would be poor in radium emanation, especially at some distance from the coast, to which place air from the land could not reach before its emanation content had largely decreased by natural decay. That this was so appeared probable from the observations of Elster and Geitel,* Simpson,† Linke,‡ and Dike,§ all of whom found air from the sea to contain much less emanation than air from the land. On the other hand observations made at Palma de Mallorca‖ and Swinemunde¶ did not give the same result; while

* 'Phys. Zeit.,' 1903, vol. 4, p. 522.

† 'Phil. Trans.,' 1905, A, vol. 205, p. 61.

‡ 'Götting. Nachr.,' 1906, p. 490.

§ 'Terr. Mag.,' vol. 13, p. 119.

‖ Elster, Geitel, and F. Harms, 'Terr. Mag.,' 1906, vol. 11, p. 1.

¶ G. Ludeling, 'Veröff. des kgl. Preuss. Meteor. Inst.,' 1905.

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Eve* made measurement over the North Atlantic Ocean, which indicated as much emanation over the centre of the ocean as he had observed in England and at Montreal. It was in the hope of reconciling these discordant results that special pains were taken to get a large amount of data during the voyage of the "Terra Nova."

The only feasible method of measuring the amount of radium emanation in the air over the sea is the one due to Elster and Geitel of exposing a negatively charged wire for two hours, and then testing it in an electroscope for induced activity. On the "Terra Nova" the wire, 810 cm. long and 0·4 mm. diameter, was stretched from one side of the ship to the other above the bridge, and this was connected by a second wire to a Braun electroscope in the small cabin which served as our physical laboratory. In order to keep the wire charged to the required negative potential (between 2000 and 2500 volts) a small influence machine was used. This was an exact copy of the "replenisher" fitted to the old form of Kelvin quadrant electrometer, but of two and a half times the linear dimensions. The "replenisher" was driven by a small spring motor which required winding every 15 minutes. Practically no difficulty was experienced in maintaining the potential even in bad weather. The insulators used throughout were of sulphur.

After the wire had been exposed for two hours it was coiled on a small aluminium frame fitting within a cylinder, 12 cm. in diameter and 10 cm. high, fixed on the top of a Wulf electroscope. The electrode of the electroscope was a small brass rod, 0·5 cm. in diameter and 9 cm. long, fitting centrally within the cylinder. The rod was charged, and then the frame holding the wire was placed around it and the cylinder closed. Five minutes after the wire had been discharged at the end of its two hours' exposure a reading of the electroscope was taken, and then further readings at intervals of five minutes. By extrapolation from these readings the loss in the first five minutes was obtained, and this was taken to be a measure of the induced activity, and so of the amount of emanation in the air.

Practically all previous observations of atmospheric radioactivity have been expressed in the arbitrary units first used by Elster and Geitel.† After exposing a wire for two hours at a potential between −2000 and −2500 volts, these physicists wound it round a cage which fitted within the instrument used by them for measuring the electrical dissipation (*Zerstreuung*). Then the activity of the air was written as 1, when 1 metre of the wire caused the potential of the electrode (*Zerstreuungskörper*) to fall 1 volt in one hour. Assuming that the active wire in our electroscope

* 'Terr. Mag.,' March, 1909.

† 'Phys. Zeit.,' 1902, vol. 3, p. 305.

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produces as great an ionisation as it would in Elster and Geitel's instrument, the same unit may be used, if we take into consideration the difference in capacity of the two instruments. The capacity of Elster and Geitel's instrument was about 15 cm., and of ours 3·9 cm.; we have calculated our results by finding the initial fall of potential caused by 1 metre of wire in one hour, and multiplying the result by 3·9/15. The values so obtained can then be directly compared with other measurements. The letter A is generally used to denote the radioactivity of the air when expressed in Elster and Geitel's units.

On the voyage from England to Melbourne 102 observations, each extending over two hours, were taken on 55 days. The mean value of A was found to be 6, the maximum value 21, and the minimum value 1. The following table gives the results of corresponding observations made on land; in each case the observations extended over 12 months:—

Observer.	Place.	A mean.	A max.	A min.
Elster and Geitel*	Wolfenbüttel (Germany)	19	64	4
A. Gockel†	Freiburg (Switzerland) ...	84	170	10
G. C. Simpson‡	Karasjok (Lapland).....	93	432	20

* 'Phys. Zeit.,' 1903, vol. 4, p. 526.
† 'Phys. Zeit.,' 1904, vol. 5, p. 591.
‡ 'Phil. Trans.,' A, 1905, vol. 205, p. 61.

From these results it seems certain that there is less emanation over the sea than over the land; but the two following observations remove any possible doubt.

On our arrival at Cape Town one of us took the instruments, exactly as they had been used on the ship, to Matjesfontain, 200 miles from the sea and 2970 feet above sea-level; 17 observations were made on six separate days. The mean value of A was found to be 124, A max. 256 and A min. 52. These values are much higher than anything observed at sea.

On leaving Melbourne for Lyttelton (New Zealand) an observation was made quite near to the land with an off-shore breeze, the value of A was 130. During the next few days the wind was from the south-west and the radioactivity fell to low values, the mean of four observations being A = 3. On nearing the west coast of New Zealand the wind fell light and came off the land, and A rose to 19 and then to 175.

A most interesting result is shown when the observations are tabulated according to latitude. As the number of observations on any one day varied from 1 to 12, it was thought best for this purpose to take the mean value

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observed on any one day, so that a single day with several observations should not outweigh other days on which only a single observation was obtained. On the journey from England to the Cape the "Terra Nova" changed her latitude rapidly, so that only a few observations could be obtained within each 10° of latitude, and consequently too much stress must not be put upon the numbers in the following table; there can, however, be no doubt that they indicate a real phenomenon:—

Latitude.	A mean.	A max.	A min.	Number of observations.
Atlantic Ocean, 40°—30° N.	7	10	4	3 obs. on 3 days.
„ 30°—20° „	9	12	8	14 „ 2 „
„ 20°—10° „	13	20	7	8 „ 3 „
„ 10°—0° „	5	8	4	6 „ 4 „
„ 0°—10° S.	6	8	5	9 „ 4 „
„ 10°—20° „	12	19	5	6 „ 4 „
„ 20°—30° „	8	11	5	7 „ 4 „
„ 30°—40° „	6	21	3	11 „ 7 „
Indian Ocean, 40° S.	3	8	1	38 „ 24 „

It will be noticed that over the Atlantic in both hemispheres the emanation increases from latitude 40° towards the Equator, but in the equatorial region itself, *i.e.* within 10° of the Equator, the emanation has a low value. The explanation of this interesting observation may probably be as follows:—

Between 30° and 40° in both hemispheres a belt of high pressure is situated in which air descends to feed the trade winds blowing towards the low pressure near the Equator. The air descending from above must be almost free from emanation owing to the short life of the latter; this no doubt accounts for the low values of A measured between 30° and 40°. As the air travels towards the Equator over the sea, it takes up emanation from the sea-water, so that the emanation content will increase in amount as the air gets further away from the place where it descended. As soon, however, as the air reaches the Doldrums it becomes thoroughly washed by the frequent heavy showers of rain, and in consequence the emanation decreases in amount. When the "Terra Nova" made her journey the Doldrums were situated to the north of the Equator and we had practically no rain between 0° and 10° S, hence the low value of A in the latter region is somewhat strange; but as stated above the number of observations was too small for details to be insisted upon.

The lowest values of all were found on the journey from the Cape to Australia, and these were no doubt due to a similar cause. The latitude on which the "Terra Nova" "ran her easting down" (about 40° S.) is south of the usual position of the region of high pressure in the South Indian Ocean;

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but as the barometer was nearly half an inch above the normal during the greater part of the journey and many calm days and days with easterly winds were encountered, it is reasonable to suppose that the region of high pressure was further south than usual, and that in consequence we were always surrounded with air which had recently descended.

As far as can be seen from the observations the radioactivity over the ocean is independent of the wind velocity, and hence of the amount of broken water—the mean value of A with winds less than force 4 on the Beaufort scales was found to be exactly the same as with stronger winds. Also no relationship between the emanation and the amount of cloud could be traced.

The amount of emanation in the air over the sea is much more constant than over the land. Day after day observations were made in the morning and afternoon with almost identical results. At the commencement of the cruise it was thought desirable to see if a daily range could be detected, and so observations were continued for 24 hours with the following result, which indicates no daily range.

June 30 and July 1.

Position at commencement ..... 26° 27′ N. 20° 48′ W.
„ end ..... 25° 07′ „ 21° 38′ „

Mean time.	A.	Mean time.	A.
hrs. mins.		hrs. mins.	
10 30	10	3 40	9
15 00	12	6 00	10
18 45	10	8 30	11
21 00	10	11 00	8
23 00	11	13 00	9
1 30	11	15 15	11

(3) *Ionisation.*

From the work of Langevin and others it appears that the air contains ions of a different kind from those first discovered by Elster and Geitel, and by Wilson. The essential difference is that while the latter have a mobility of about 1 cm./sec. in a field of 1 volt/cm. the former have a mobility of 1/300th part of this. There is a sharp demarcation between the two kinds of ions, for under normal conditions the air does not contain ions having specific mobilities between 0·2 and 0·0003 cm./sec. The instrument originally designed by Ebert for measuring the ionisation of the air takes account only of the faster moving ions, and these are by far the most important in the phenomena of atmospheric electricity. It is with these ions only that we are concerned in this paper.

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The instrument used on the "Terra Nova" was the newest form of Ebert's instrument made by Günther and Tegetmeyer. In it the tube which forms the outer electrode of the cylindrical condenser for withdrawing the ions is vertical and of 3 cm. diameter. The inner electrode is a brass rod 141 cm. long and 0·5 cm. in diameter, and fits directly on to a Wulf electrometer. The aspirator is of the usual form supplied by this firm. When working, 91·7 litres of air pass the condenser in a minute, the electrical capacity of the condenser being 17·4 cm. According to the makers it is only necessary for the instrument to run for 5½ minutes in order to get a satisfactory determination of the ionisation. Experience showed, however, that a really satisfactory observation could not be made under 33 minutes, and most of our observations extended to 44 minutes.

Our usual method was to charge the instrument with positive electricity and leave it for half an hour or so without the aspirator running in order to determine the insulation leak. The aspirator was then set in motion and when the bell attached to the revolution counter rang a reading was taken. After each 2500 turns of the fan the bell rang again, and the instrument was wound up. After the bell had rung six times (about 11 minutes after starting) a reading of the electroscope was taken. The observation was continued for another similar interval and then again for a third. If the three readings were in good agreement, the instrument was discharged and recharged with negative electricity. If, however, the readings did not agree well the observation was continued for a fourth interval. In the same way a measurement was made with a negative charge on the condenser, and afterwards the observation with positive charge was repeated. Thus each complete observation (leaving out the period of insulation test) extended over a period of between 1 h. 40 m. and 2 h. 15 m. Only those observations have been used in the following discussion in which the complete sequence as just sketched was carried out. With the Wulf electroscope good observations were possible even when the ship was rolling to a considerable extent.

Owing to unforeseen difficulties, satisfactory determinations of the ionisation were not obtained until the "Terra Nova" had crossed the Equator and reached 10° S. latitude. From then until our arrival at Melbourne observations were taken whenever the weather permitted. During the voyage 35 complete measurements were obtained and the mean results are shown in the following table, in which I_+ stands for the quantity of positive ions contained in a cubic metre of air expressed in electrostatic units, I_- the corresponding quantity of negative ions, and q the ratio I_+/I_-.

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	I_+.	I_-.	q.
E.S. units per m.^{3}	0·37	0·31	1·21

Before comparing these results with others it will be as well to discuss them in more detail.

Ionisation and Latitude.—In the Atlantic Ocean there appeared to be a distinct dependence on latitude, which seems to confirm the explanation already given for the geographical distribution of the radioactivity.

Latitude.	I_+.	I_-.	q.	Number of observations.
Atlantic Ocean, 10°—20° S.	0·30	0·22	1·36	(3)
„ „ 20°—30° S.	0·36	0·30	1·18	(8)
„ „ 30°—40° S.	0·39	0·35	1·10	(4)
Indian Ocean 40° S.	0·39	0·32	1·22	(20)

From 10° to 40° S. the ionisation increased and q decreased. If the air descends between latitudes 30° and 40°, as suggested, it would be free from dust, and the ionisation could be high even though there was only little emanation in the air. As the air travelled northwards in the trade winds it would become loaded with minute salt particles obtained from the sea; in consequence, the ionisation would decrease, and the value of q increase. In the Indian Ocean we sailed the whole way within a degree or two of 40° S., so it was impossible to test for a similar variation with latitude. The above remarks have been made by way of suggestions only, the observations being far too few to be relied on with any certainty.

Ionisation and Temperature.—The observations have been tabulated according to temperature, with the following result:—

Temperature.	I_+.	I_-.	q.	Number of observations.
< 10° C.	0·36	0·30	1·22	10
10° C.—20° C.	0·40	0·34	1·18	16
> 20° C.	0·34	0·27	1·23	9

Experiments on land have shown a marked increase of ionisation with increase of temperature; the experiments on the sea indicate the same with the exception of higher temperatures. As the latter were only met with in the trade winds (10° to 27° S.) the burdening of the air with salt may well have counterbalanced the effect of temperature.

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Ionisation and Wind.—The higher the wind the more the air is filled with spray, blown off from the tops of the waves. Two effects might be expected from such breaking of the water: (1) One might expect from the Lenard effect an increase in the number of positive ions, as the splashing of salt water is known to be accompanied by the generation of positive ions; (2) the large amount of spray and salt might decrease the total ionisation, just as fog and dust have been proved to do. A division of the data according to wind strength indicates the latter effect, for, as the following table shows, both the ionisation and the ratio q are less with high winds than with light winds:—

Beaufort numbers.	I_+.	I_-.	q.	Number of observations.
0, 1, 2, and 3	0·40	0·33	1·23	16
4, 5, 6, and 7	0·35	0·30	1·18	18

The value of the ionisation measured on this voyage agrees fairly well with the only two other sets of observations made over the ocean. Eve, in a journey from Canada to England,* found $I_+ = 0{\cdot}33$, $I_- = 0{\cdot}26$ and $q = 1{\cdot}24$. Boltzmann† found over the Atlantic Ocean $I_+ = 0{\cdot}39$, $I_- = 0{\cdot}27$, $q = 1{\cdot}53$.

The ionisation over the land is so dependent on meteorological conditions that it is difficult to choose data to compare with our results. Perhaps the most suitable are those of one of us observed in Karasjok, in Lapland. At that place the ionisation was found to depend very largely on temperature and the results of observations at temperatures comparable with those encountered on the "Terra Nova" are shown in the following table:—‡

Karasjok (Lapland).

Temperature °C.	I_+.	I_-.	q.
5—10	0·45	0·40	1·12
10—15	0·45	0·43	1·05

These numbers are higher than those obtained over the ocean, and there can be little doubt from them and other observations made on land that

* 'Phil. Mag.,' 1907, vol. 13, p. 248.
† 'Phys. Zeit.,' 1905, vol. 6, p. 132.
‡ Simpson, 'Phil. Trans.,' 1905, A, vol. 205, p. 61.

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the ionisation over the sea is less than that over the land under similar meteorological conditions.

(4) *Ionisation of the Air in Closed Vessels as Measured over the Surface of the Ocean.*

This work was undertaken with a two-fold object in view:—(1) To determine the factors governing the variations of the ionisation in closed vessels, and particularly to investigate a possible variation due to greater or smaller quantities of radium products in the atmosphere; (2) to throw further light on the origin of this "natural ionisation," and, if possible, to determine its absolute value.

The conditions obtaining on the "Terra Nova" were particularly favourable to such work: (1) Because the sea not only contributes an inappreciable effect to the observed ionisation, but also screens off the uncertain effect of the radiations from the earth's solid crust, which is the predominating factor in measurements made on land; (2) on account of the ship's age, which might reasonably be expected to imply a greater freedom from radioactive substances than is the case with less old ships.*

Apparatus and Method of Measurement.—The ionisation vessel used in all the experiments was a zinc cylinder having a volume of 26,500 c.c. Previous work has shown that zinc vessels are not subject to the increase of ionisation in the course of time, which takes place with cylinders of lead and possibly other metals,† and zinc has also the advantage of giving a low absolute value for the natural ionisation.

The cylinder was cleaned in April, 1910, by sandpapering and washing with hydrochloric acid, ammonia, alcohol, and distilled water, and dry dust-free air immediately introduced. After this the cylinder was closed, but not hermetically sealed.

A glance at the accompanying diagram (fig. 2) will show the method of measurement. The cylinder A‡ was insulated by the ebonite pegs B, and the ebonite collar C, and kept at a high and constant potential by a battery of small dry cells sufficient to give a saturating voltage. These cells,§ 50 in number, were embedded in paraffin wax, and weighed about 20 lbs., and throughout the whole series of observations acted in a most satisfactory manner. The electrode E was screwed into the rod carrying the quartz fibres of a Wulf electroscope.

* Wright, 'Phil. Mag.,' February, 1909, p. 310.

† McLennan, 'Phil. Mag.,' December, 1907.

‡ In the figure the cylinder A is shown much smaller relative to the electroscope than it was in reality.

§ Furnished by the Ecco Battery Co., Bow Common Lane, London, E.

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In making a measurement, the cylinder A and the insulated inner case G of the electroscope are connected to the positive terminal of the dry cells. By pushing in the key D, and then withdrawing it, the electrode is earthed, and the quartz fibres deflected. In the course of time this deflection decreases, and the rate of decrease (about 10 volts per hour) gives a measure of the ionisation current. As the rate of decrease during the second hour was always appreciably the same as during the first, no correction has been applied for defective insulation.

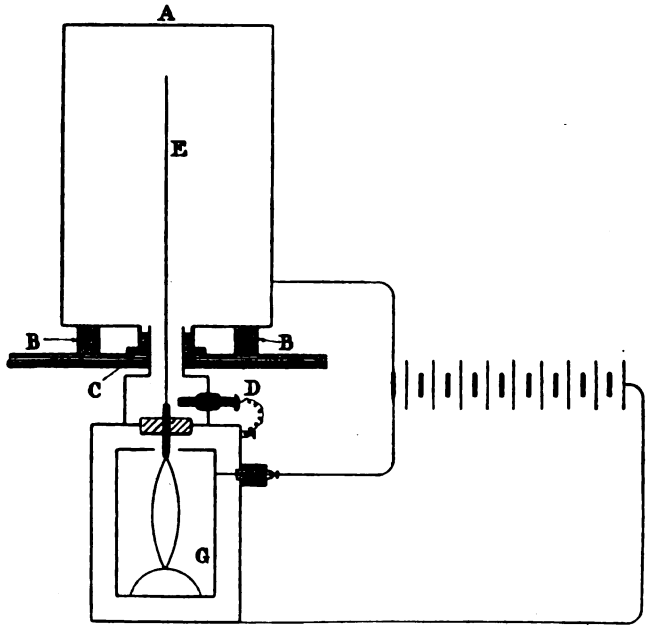

Fig. 2.

The capacity of the electrode system is found by applying a known potential to the inner case G, and noting the potential to which the electrode system is raised. A repetition of this proceeding with a known capacity then readily gives all the data required for determining the capacity of the whole system. The error of any single observation (duration one hour) may be put down as 3·5 per cent., depending on the amount of the ship's motion. A typical set of readings for a complete 24 hours is given in Table II.

In Tables III, IV, and V are shown the analyses of the results from Madeira to Melbourne (Australia); the former series being marked "A" and the latter "B." The suffix numbers represent the number of observations used in calculating the mean value. The total number of hourly observations was about 250.

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Table II.

September 24, 1910. Mean time.	Ions per c.c. per sec.	September 25, 1910. Mean time.	Ions per c.c. per sec.
h. m.		h. m.	
9 30	6·3	0 30	6·5
10 30	6·2	2 30	7·0
11 00	6·4	4 30	6·9
12 30	6·4	5 30	6·8
17 30	6·6	7 30	6·9
19 30	6·8	9 00	6·2
21 00	6·7	11 00	6·3
22 00	6·8	12 30	6·4
23 00	6·6		

Capacity of system = 9·4 cm.

Table III.

Time of day.....	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
q (A).....	6·5 (1)	6·4 (1)	6·3 (2)	—	6·4 (2)	6·1 (1)	5·9 (1)	6·6 (3)	6·5 (11)	6·3 (18)	6·4 (19)	6·4 (8)
q (B).....	—	6·5 (1)	—	7·0 (1)	6·9 (1)	6·8 (1)	6·9 (1)	—	6·3 (11)	6·2 (22)	6·2 (16)	6·3 (19)

Time of day.....	13.	14.	15.	16.	17.	18.	19.	20.	21.	22.	23.	24.
q (A).....	6·5 (13)	6·7 (11)	6·4 (12)	6·5 (10)	6·5 (9)	6·4 (7)	6·4 (5)	6·4 (1)	6·4 (2)	6·0 (2)	6·3 (2)	6·0 (1)
q (B).....	6·3 (17)	6·1 (18)	6·2 (13)	6·3 (9)	6·4 (3)	6·9 (1)	6·6 (2)	6·9 (1)	6·6 (2)	6·8 (1)	6·6 (2)	6·5 (1)

Table IV.

A = radv. of air ...	0-5.	5-10.	10-15.	15-20.	20-25.	25-30.	30-35.	35-40.	40-45.	45-∞.
q (A)	—	6·4 (2)	6·7 (5)	6·2 (2)	6·4 (7)	6·7 (2)	—	—	6·0 (1)	6·4 (3)
q (B)	6·1 (4)	6·3 (11)	6·2 (5)	5·7 (1)	6·2 (1)	—	—	6·5 (1)		

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Table V.

	q (A).	q (B).
Barometer over 30·2 inch	6·36 (8)	6·15 (13)
,, under 30·2 inch	6·70 (12)	6·40 (12)

It may be noted (Tables III and IV) that evidence of a regular daily variation or of any connection between the observed ionisation and the radium-content of the air is quite lacking. No certain connection, moreover, was found with air temperature, sea temperature, rainfall, or quantity of coal in the adjacent bunkers.

Though in individual cases no relation between ionisation and pressure could be traced, still a fairly definite and well-marked connection was shown when the mean of all observations was taken (Table V), a high barometer corresponding to a low value of q.

Though in general the observed variations were within a few per cent. of the mean value, still on several occasions, when the ship was close to land, appreciably higher numbers were obtained. Thus, when anchored off South Trinidad Island, the value of q rose from 6 to 8, dying away to the former value a few hours after leaving the island. Unfortunately, no observations on the radium-content of the air were taken while anchored off the island.

Again, at Melbourne, the ionisation rose from 6·5 to 9, falling again to 6·8 about twenty hours after reaching the open sea. Simultaneously with the occurrence of this high value was recorded a value for the radioactivity of the air, A = 130, but the high ionisation persisted for some time after the air radioactivity fell again to A = 3.

On another occasion, when nearing New Zealand (the cylinder having been recleaned in the meantime), the value of q changed from 4 to 5, and returned to 4 thirty-six hours afterwards. Concurrent with this high value, the radium-content of the air was represented by A = 175, though again the high ionisation persisted for some twenty-four hours after A had fallen to its normal value.

Possibly the most interesting feature of the series of observations is the lack of any regular daily variation in the natural ionisation over the ocean; for though Gockel,* Wright,† and Cline‡ have been unable to detect any

* Gockel, 'Phys. Zeit.,' 1908, vol. 9, p. 907.

† Wright, 'Phil. Mag.,' February, 1909.

‡ Cline, 'Bull. Roy. Soc. Canada,' October, 1909.

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variation whatever over the land, many observers, including Wood and Campbell,* Strong,† and Wulf‡ have found fairly large variations.

As a result of their investigations, Campbell and Wood have found a double daily period in the natural ionisation, whose maxima and minima correspond with the maxima and minima of the earth's potential gradient. The generally accepted explanation for this correspondence is that the radioactive products in the atmosphere have a greater tendency during high positive gradients to be deposited on the earth's surface than during low or negative potential-gradients, and may thus reinforce the penetrating radiation from the earth.

A simple calculation shows what effect might be expected from an annihilation of the RaC in the atmosphere.

Taking

Q = Ra equivalent in air§ = 10^{-16} grm. per c.c.,

K = number of ions generated per c.c. per sec. in a zinc vessel by 1 grm. Ra at 1 cm. distance,‖

q = number of ions in the vessel due to RaC in air,

λ = coefficient of absorption of air = 0·00004, and

r = distance from the cylinder,

we have

$$q = 2\pi KQ \int_0^\infty \frac{r^2 \cdot e^{-\lambda r}}{r^2} dr,$$

$$= 2\pi \frac{KQ}{\lambda} = 0{\cdot}05.$$

It is therefore clear that variations in the penetrating radiation from the RaC in the atmosphere cannot be the cause of the observed variations.

Of more importance, possibly, will be the deposition of RaC on the ground, corresponding to a decrease in the radium-content of the air. Let us assume that all the RaC in a layer of air 1 kilometre thick is suddenly deposited on the earth's surface, supposed flat, and, in order to simplify calculations, let us assume that λ-air = zero.

Ra equivalent on earth's surface = 10^{-11} grm. per sq. cm.

Then
$$q = \int_{100}^{100,000} KQ \frac{2\pi r \cdot dr}{r^2} = 2\pi KQ \Big[\log_e r\Big]_{100}^{100,000},$$
$$= 1{\cdot}9,$$

* Campbell and Wood, 'Phil. Mag.,' 1907, [6], p. 2.

† Strong, 'Phys. Zeit.,' 1908, vol. 9, p. 117.

‡ Wulf, 'Phys. Zeit.,' 1909, vol. 10.

§ Eve, 'Terr. Mag.,' March, 1909; Satterly, 'Phil. Mag.,' July, 1910.

‖ Eve, *loc. cit.*

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taking the electroscope as 1 m. from the ground and assuming that only that surface within a kilometre will affect the air in the cylinder.

There is thus a possibility that the RaC carried down in this way may produce a measurable effect on the ionisation. Probably a more efficacious agent than the earth's potential gradient, in depositing radioactive products on the ground, would be the occurrence of heavy rain storms, and the consequent carrying down of the products by the falling rain. Though observations connecting natural ionisation with rainfall are few in number, still Mache and Rimmer,* and Gockel,† have found that the ionisation increases sometimes as much as 100 per cent. after a heavy thunder shower.

Though effects of this magnitude may be possible over or near the land, it may well be expected that such causes will have little or no effect on the natural ionisation over the sea, chiefly because the radium-content of sea air is distinctly smaller than that of land air, but also because any radioactive product deposited upon the sea surface will go into solution and be quickly disseminated.

That the variations noted by certain observers on land are really due to variations in the amount of radioactive products present on the ground in the vicinity of the observing station can now no longer be doubted, though it may well be that in certain places these variations are too small to be measurable.

Thus it was seen that near land a high radioactive-content of the air almost synchronised with a high natural ionisation. That this high ionisation is due to radioactive products deposited on the ship itself is highly probable from the fact that the ionisation persisted for some time after the high air radioactivity had disappeared. It may also be deduced from the slow rate of decrease that thorium products, in at least some cases, played a considerable part.

Absolute Value of the Natural Ionisation.—Many efforts have been made during late years to reduce the number of ions generated in metal vessels to their lowest possible number, both by careful cleaning of the vessel to free it from radioactive deposits on the walls, and by screening from the earth's penetrating radiation.

The lowest value of q yet obtained (and as yet unpublished) for an unscreened vessel over the land is 8 ions. This number was found in a zinc cylinder of length 60 cm. and diameter 24 cm., the vessel being under observation in the new wing of the Cavendish Laboratory at Cambridge. The cylinder, after the most careful cleaning, was filled with dry dust-free air, which had been slowly passed through a worm immersed in liquid air, and also through a brass tube with a coaxial wire charged to a high

* Mache u. Rimmer, 'Phys. Zeit.,' 1906, vol. 7, p. 617.

† Gockel, 'Phys. Zeit.,' November, 1909.

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potential, in order to make sure that no radium emanations or products were admitted with the air.

Still lower values of q have been obtained by screening the vessel from the earth's penetrating rays. Among those who have attempted such "screening" experiments may be mentioned Cook,* McLennan and Burton,† Wright,‡ and Gockel.§ These experiments show that water furnishes the best natural screen against the penetrating rays from the earth. Thus, over the ice of Toronto Bay (Lake Ontario) the very low value of $q = 4{\cdot}4$ ions (recalculated for $e = 4{\cdot}6 \times 10^{-10}$) was obtained in a zinc cylinder of approximately 27 litres capacity, this number being a decrease of 5·5 ions from the value obtained in the laboratory.

In the present series of observations it was therefore thought advisable to compare the measurements made over the sea with similar observations on land, and with observations in a small skiff, in order to eliminate the possible effect of radioactive impurities in the hull of the "Terra Nova." The results are given in Table VI, and show a difference between land and sea values of about 6 ions.

Table VI.

Position.	q.	Difference between land and sea.	Remarks.
"Terra Nova," Simon's Bay ...	6·3	—	In laboratory.
Matjesfontein	12·3	6·0	1·5 m. from ground (in open).
"Terra Nova," Lyttelton	6·3	—	At dock.
Small skiff	4·1	2·2	In open bay, 100 m. from breakwater.

Now since the mean quantity of Ra in the sea-water is $Q = 1{\cdot}6 \times 10^{-14}$,‖ a simple calculation shows that the number of ions in the cylinder due to this agency is $q = 0{\cdot}005$.

We may therefore safely say that over the sea the number of ions in the cylinder due to penetrating rays from terrestrial sources (air, land, and water) is not more than 0·1. Thus the number in Column 3, Table VI, represents within 0·1 ion that part of q due to the radioactive substance in or on the soil at the position of observation.

Moreover, by the observations in the small skiff, we have obtained the low value of 4·1 ions per cubic centimetre per second in this zinc cylinder

* Cook, 'Phil. Mag.,' 1909, [6], vol. 7, p. 140.

† McLennan and Burton, 'Phil. Mag.,' 1903, [6], vol. 5, p. 707.

‡ Wright, *loc. cit.*

§ Gockel, 'Phys. Zeit.,' November, 1909.

‖ Joly, Presidential Address, Brit. Assoc., Dublin, 1908.

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a number almost exactly the same as that obtained a few days previously on the "Terra Nova" in the open sea, after the cylinder had been cleaned again, and when the ship was presumably free from radioactive deposits.

It will be seen that in this case, as with all previous attempts to reduce the value of q by screening the ionisation vessel from the earth's penetrating radiation, there remains a residual ionisation due to causes other than penetrating rays from terrestrial sources.

Three possible contributors to this residual ionisation need alone be considered here:—

(1) Emanation within the vessel and admitted with the gas.

(2) Intrinsic radioactivity of the metal or radioactive impurities in it.

(3) Spontaneous ionisation or breakdown of the enclosed gas.

(1) *Radioactive Emanation in the Gas.*—A calculation from known data of the number of ions due to and particles shot out from Ra Em. and other radium products present in the cylinder and admitted with the air shows, on the assumption that all α-particles are totally absorbed in the gas, and that the amount of Ra Em. in the air is 10^{-16} grm. per cubic centimetre,* that in the mean 1·3 ions alone may be put down as due to emanation in the air of the vessel. Experiments, however, have shown that admitting the air slowly through a spiral immersed in liquid air has caused no diminution in the observed value of q, and it would seem possible that the filtering of the air through cotton wool extracted all the emanation.

(2) *Radioactivity of Metal or Radioactive Impurity in it.*—The belief in the possibility of an intrinsic activity of all metals, and in the possibility of radioactive impurities, has been considerably strengthened since the discovery of the radioactivity of potassium and rubidium, and the separation of a radioactive substance (RaF) from samples of commercial lead. In this connection it might be well to point out that lead is the metal with which the rise in conductivity in the course of time is most marked, and that those metals, as zinc, which show no rise may reasonably be supposed free from impurities. It would therefore seem probable that our zinc vessel was at least free from radioactive impurity.

(3) *Spontaneous Ionisation of the Gas.*—The possibility that the residual natural ionisation may be due to a spontaneous breakdown of the gas is one which has of late received but scant attention. Calculations have, indeed, been made† to show that the mechanical shock in the collisions of gas molecules, by virtue of their kinetic motion, is quite insufficient to account for the production of the required 4 ions per cubic centimetre per second.

* Eve, 'Terr. Mag.,' March, 1909.

† Karl Bergwitz, F. Vieweg u. Sohn, Braunschweig, 1910.

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This calculation, however, is on the assumption that the kinetic energy of motion is directly convertible into the electrical energy within the atom.

Since, however, it is known that the metal rubidium* is capable even in the dark of emitting electrons from itself, it appears by no means certain that gaseous molecules have not the same property to a greater or less extent. On this view we might well expect that a heavy gas with many electrons would be more easily ionised than a light one. Jaffé† has, indeed, shown that for nickel carbonyl the natural ionisation is about five times that of air, and for hexane‡ an even larger number (12·6) is recorded.

In further support of the theory of a spontaneous ionisation in gases is the fact that each observer has found the same values for q in vessels of all metals except those of lead, which alone is known to contain a radio-active impurity.

We see also that on this view the relation between air pressure and residual ionisation will be a linear one,§ the value of q depending only on the number of molecules within the vessel. The small changes in ionisation due to changes of barometric pressure, however, would usually be masked by other factors called into play by these changes.

It is probable that a careful series of observations on the relation between pressure and q in a perfectly screened cylinder might well prove the truth or falsity of the theory of a spontaneous ionisation of the gas, and in any case can hardly fail to give valuable information regarding the origin of the residual ionisation in closed vessels.

The results of the observations on natural ionisation may be stated as follows:—

(1) No regular daily variation has been found over the sea.

(2) A slight dependence of the natural ionisation upon barometric pressure has been observed—a high barometer giving a low value of q.

(3) The number of ions in a zinc cylinder due to penetrating radiation from the soil at Matjesfontein has been found to be 6.

(4) It has been found that a considerable addition ($q \doteq 3$) to the normal ionisation, as measured on the ship, may be contributed by radio-active products deposited on the ship, and due primarily to a high value for the radium-content of the air.

(5) The lowest number of ions per cubic centimetre per second observed in a closed zinc cylinder of 27 litres capacity over the sea is 4.

* Sir J. J. Thomson, 'Conduction through Gases,' p. 251.

† Jaffé, 'Phil. Mag.,' October, 1904, p. 556.

‡ Jaffé, 'Ann. d. Phys.,' February 4, 1909, vol. 28, (2), p. 326.

§ Burton, 'Phys. Rev.,' 1904, vol. 18, p. 3.

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On the Ionic Solubility-product.

By JAMES KENDALL, M.A., B.Sc. (Vans Dunlop Scholar in Chemistry, University of Edinburgh).

(Communicated by Prof. James Walker, F.R.S. Received February 16,—Read March 9, 1911.)

The theory of a constant ionic solubility-product was first advanced by Nernst,* from the analogy of the laws governing dissociation in gases. According to the principle of mass action, if the dissociation pressure of a system in equilibrium be changed by the introduction of an excess of either of the dissociated gases, combination takes place between them until equilibrium is restored. Thus, on the addition of either NH_3 or HCl to a system consisting of ammonium chloride in equilibrium with its dissociation products, ammonium chloride is produced. For each temperature, the product of the pressures of NH_3 and HCl is a constant. Similarly, Nernst found that the solubility of an electrolyte in water was reduced by the addition of any salt containing a common ion. The variations in the solubility of silver acetate (a sparingly soluble salt) in water containing known amounts of silver nitrate or sodium acetate were investigated, and the results obtained confirmed the view that a corresponding equilibrium law was here applicable. If we confine ourselves to substances of the simplest type RX, the law may be stated thus: "At a given temperature the solubility of a sparingly soluble electrolyte is dependent upon a constant, which is proportional to the product of the concentrations of the ions of the electrolyte."

The fundamental assumption made in the application of this law is that in a saturated solution of an electrolyte the undissociated salt in solution plays the part of an intermediary between the ions and the solid, being in equilibrium with the ions on the one hand and with the solid on the other. Consequently, so long as the solvent remains the same, the concentration of the undissociated salt is constant, however much the ionic concentrations may be separately varied by the introduction of other electrolytes; and the product of these ionic concentrations is also a constant.

Expressed algebraically, if s be the concentration of the saturated solution and m the degree of dissociation, m^2s^2 represents the solubility-product, and $(1-m)s$ the "constant undissociated value." These are connected, by the law of mass action, through the equation

$$m^2s^2 = (1-m)s.c,$$

where c is the dissociation constant.

* 'Zeits. physikal. Chem.,' 1889, vol. 4, p. 372.

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The theoretical solubilities of two substances containing a common ion in the presence of each other in aqueous solution, may now be established. Let a^2 and b^2 be their solubility-products, x and y their ionic concentrations in simultaneous solution. Then we have

$$x(x+y) = a^2, \quad y(x+y) = b^2,$$

$(x+y)$ being the concentration of the common ion. From this quadratic x and y are at once obtained.

If one of the substances is present not as a solid, but as a solution in water of known concentration s, the equations become

$$x(x+y) = a^2, \quad \frac{y(x+y)}{s-y} = c,$$

where c is the dissociation constant of the substance in solution. From these equations a cubic results, whence x and y are obtainable by trial.

In the above equations Ostwald's dilution law has been assumed, namely, that c is a constant for each particular electrolyte. This is true only in the case of weak acids and bases; for the majority of substances, the strong electrolytes, c is not constant, but increases with increase of concentration. Thus, with increase of concentration, the ratio of the ionised to the total substance dissolved becomes greater than the theoretical. The values of c for such a substance, however, can be determined for each concentration, and the value at saturation used to find the solubility-product. Noyes,* indeed, has used the values thus found not only for solubility determinations such as are indicated above, but also for the reverse problem of determining the degree of dissociation of a second substance by the solubility method.

The above assumption of a constant undissociated value has been attacked both theoretically and experimentally by Arrhenius.† Arrhenius showed that the assumption has no sound theoretical basis, and on determining the solubilities of silver salts of certain organic acids in water and in aqueous solutions containing excess of the corresponding sodium salts, he found that the undissociated value was not constant, but decreased with increase of concentration.

These results of Arrhenius have been investigated by Stieglitz.‡ Stieglitz, comparing this decrease of the undissociated part with the ratio of the ionic to the total strength, which, as mentioned above, increases beyond theoretical with increase of concentration, has formulated the hypothesis that the two

* 'Zeits. physikal. Chem.,' 1892, vol. 9, p. 603.
† 'Zeits. physikal. Chem.,' 1899, vol. 31, p. 197.
‡ 'Journ. Amer. Chem. Soc.,' 1908, vol. 30, p. 946.

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effects counterbalance each other, and consequently restates the theory of the constant solubility-product in an empirical form. But the results of Arrhenius, as worked out in the above paper, give divergences in the solubility-product of from 5 to 10 per cent., and so long as such divergences exist unexplained, the theory can hardly be regarded as even empirically established; it remains no more than an approximation.

Previous investigations upon the simultaneous solubilities in water of two substances containing a common ion have been confined to those cases in which the substances examined have been of the same type, *i.e.* either both strong or both weak electrolytes. The case of two strong electrolytes has been most frequently examined, the special interest here lying in the question whether the law of mass action is, or is not, applicable. Fewer instances of the simpler case of two weak electrolytes have been investigated, but, in both types, the hypothesis of the constancy of the solubility-product has been considered to give results consistent with those obtained experimentally, although, even in dilute solutions, the agreement is only approximate. For instance, in a solution saturated simultaneously with thallium chloride and thallium bromate, the product of the ionic concentrations of each was found to be increased by about 5 per cent.* The saturated solutions of each of the above salts are (approximately) only one-fortieth normal.

No experiments, however, have been made with two substances of opposite types—one strong and one weak electrolyte—and the primary object of the following research was to supply this deficiency. Here also arises the question of the applicability of the law of mass action. In preliminary experiments divergences from the theoretical result of several per cent. were obtained, similar to that given above. In parallel experiments on the two types already investigated even larger differences were observed, far exceeding the limits of experimental error. Finally a series of experiments on all the possible types of combination of two electrolytes was carried out, first with dilute and afterwards with more concentrated solutions, in order to ascertain the cause of these divergences, and more especially to discover whether they formed an inherent defect in the theory or could be explained away on other grounds.

Experimental.

The substances used were acids of the simple type HX. Weak electrolytes: salicylic acid, $C_6H_4(OH).COOH$; ortho-nitrobenzoic acid, $C_6H_4(NO_2).COOH$; hippuric acid, $NH(CO.C_6H_5).CH_2.COOH$; formic acid,

* A. A. Noyes, 'Reports of Congress of Arts and Sciences, St. Louis,' vol. 4, p. 322.

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H.COOH; acetic acid, $CH_3.COOH$; and malonic acid, $CH_2(COOH)_2$. (The last named was used only in such concentrations as allowed it to be considered as a monobasic acid, splitting up into the ions $CH_2\begin{matrix}COO'\\COOH\end{matrix}$ and $H^{\bullet}$). Strong electrolytes: hydrochloric acid; picric acid, $C_6H_2(OH)(NO_2)_3$; and trinitrometacresol or methyl picric acid, $1:3:2:4:6\text{-}C_6H(CH_3)(OH)(NO_2)_3$.

The solid acids were purified by recrystallisation from freshly-distilled water; small crystals suitable for the experiments being obtained by rapid cooling from a hot saturated solution. Samples tested gave sharp and distinct melting points. The liquid acids were purified by distilling, and rejecting the first and last portions of the distillate. In all cases solutions were made up with freshly-distilled water, and the glass vessels employed were well steamed out before first using.

The concentrations of the saturated solutions of certain of the above acids at 25° C. were first determined. A few grammes of the acid were placed in a glass-stoppered bottle, half filled with water; over the neck of the bottle a square of rubber sheeting was tied tightly, and the bottle was then clamped in the stirrer of a thermostat and rotated for several days. A measured quantity (25 to 100 c.c., according to the strength of the solution) was then removed by means of a pipette, the body of the bottle remaining in the thermostat. To the end of the pipette was fitted a filter-cover, to prevent the entrance of any crystals, and the pipette itself, when not in use, was kept in a glass tube immersed in the thermostat, so that it was at the same temperature as the solution, and no crystallising occurred inside it. The solution was titrated immediately against baryta, phenolphthalein being used as an indicator. The bottle was again circulated in the bath, and the solution tested every few days until a steady value was reached.

Another method, used for single acids only, was to make a saturated solution above 25° C., add a nucleus of crystals, and rotate in the thermostat as before until a constant titre was obtained. The true concentration of the saturated solution at 25° C. was thus approached from both directions.

Limits of Error.—The above experiments were performed in duplicate; divergences rarely exceeded 0·2 per cent., and were never greater than 0·4 per cent. The two methods also gave results agreeing well within this limit.

The temperature of the thermostat was maintained within 0°·1 C. of 25° C. The thermostat being very large, any change of temperature was correspondingly slow.

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The baryta solution used, approximately 1/40 normal, was standardised against each of the acids. The different values obtained varied by less than 0·2 per cent. This, besides testifying to the purity of the acids used, allowed the employment of one mean value, greatly simplifying the calculations in subsequent experiments. With picric and methyl picric acids, the end point was at first difficult to distinguish, owing to the disturbing colour effect, but after some practice the first permanent change of tint could be detected quite accurately by using a comparison solution.

In most cases the saturation point was soon reached; methyl picric acid, however, attained its full value only after two months, picric acid not even then. It was found that the presence of a few drops of ligroin or benzene in the solution shortened the necessary time for methyl picric to a few days, but the end points reached differed from that obtained with pure water. Ligroin, in which the acid is moderately soluble, increased its solubility by 2 per cent.; benzene, in which it is freely soluble, by 6 per cent. A considerable difference was thus caused by the presence of the extremely small amounts of each in solution in the water. This is noteworthy in view of results afterwards obtained.

In Table I below the concentrations of the saturated solutions of the acids are given in normalities; from these, by means of the dissociation constant, the solubility-product and the "constant undissociated value" of each acid are obtained.

Table I.—Solubilities of Single Acids.

Acid.	Solubility.	Solubility product.	"Constant undissociated value."
Salicylic	0·01634 N	0·0000130	0·01273 N
o-nitrobenzoic	0·04360 N	0·0001849	0·03000 N
Methyl picric	0·01000 N	0·0000846	0·00080 N
„ (ligroin present)	0·01019 N	—	—
„ (benzene present)	0·01059 N	—	—
Hippuric	0·02048 N	0·0000041	0·01846 N

The following dissociation constants* were used above, and in calculating the theoretical results of subsequent experiments:—

Salicylic acid	0·00102	Formic acid	0·000214	Hippuric acid	0·000222
o-Nitrobenzoic acid	0·00616	Malonic acid	0·00158		

It was necessary to determine specially the values given above in the case of methyl picric acid, since the molecular conductivities of the acid and of its sodium salt had not been previously tabulated.

* Ostwald, 'Zeits. physikal. Chem.,' 1889, vol. 3, p. 418.

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Molecular Conductivity of Methyl Picric Acid.

The sodium salt was first obtained by adding the requisite volume of sodium hydroxide solution (freshly prepared from metallic sodium and standardised by methyl picric acid) to a known weight of methyl picric acid. On evaporating the liquid to small bulk crystals were obtained, which were recrystallised from water and alcohol. Sodium picrate was also prepared by a similar method.

The values for the molecular conductivities obtained from these salts, however, were obviously too low. The salts were finally found to consist of a hydrate, the water from which could not be expelled under 100° C. Owing to their explosive nature it was inadvisable to heat the salts above this temperature.

By neutralisation, as before, and then direct addition of the requisite volume of water to bring the solution to N/32, solutions were obtained giving the following values for the molecular conductivity. Those for sodium picrate, given for comparison, are practically identical with Ostwald's values for that salt.*

v.	Sodium picrate.	Sodium methyl picrate.
32	72·9	71·3
64	76·1	73·4
128	78·1	75·2
256	79·7	76·9
512	81·2	78·6
1024	82·6	80·0
Whence—		
∞	85·7	83·1

The above results are the mean values of two determinations. Taking the values Na = 51·0, H = 349·5 (the mean of the values given by Ostwald and Kohlrausch), we obtain, for the maximum molecular conductivities of the acids, the values 384·2 and 381·6 respectively.

The molecular conductivities of the acids themselves were then determined, and are given below, together with the values of the degree of dissociation (m) obtained therefrom :—

v.	Picric acid.	*m.*	Methyl picric acid.	*m.*
32	343·4	0·894	—	—
64	354·9	0·924	—	—
128	360·7	0·939	352·9	0·925
∞	384·2	1·0	381·6	1·0

* 'Allg. Chemie,' 1893, vol. 2, p. 751.

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By drawing the curves of the values of m given above we obtain, by extrapolation, for N/100 methyl picric acid (the saturated strength at 25° C.) the value $m = 0{\cdot}92$. From this the solubility product and the "constant undissociated value" are obtained.

The above values for the molecular conductivities of the acids are in general agreement with those given for picric acid by Ostwald* and Rothmund;† but the degree of error may be fully 1 per cent. This would affect the degree of dissociation to the same extent; but, by trial from the equations, it was found that an error of 5 per cent. was required to affect the solubility determinations, afterwards made with the acids, beyond the limits of experimental error.

The conductivities were determined with a rotating commutator and galvanometer, more satisfactory results being obtained with this apparatus than with the usual induction coil and telephone, especially for the more dilute solutions.

In the determination of the solubility of one acid in the presence of another, the method of procedure was exactly similar to that already described for single acids. The experiments were of two classes: in the first, two solid acids were taken with water; in the second, one acid was present as a solid, the other as a solution in water of known strength. In all cases the end point was quickly reached, even methyl picric, in the presence of another acid, attaining the steady state in a few days.

The first investigations were of the simplest type, the two acids obeying Ostwald's dilution law. Of these, salicylic and *o*-nitrobenzoic acids are good examples, and a full series of experiments with these two acids was carried out, the results of which are shown in Table II (p. 207). Since they serve to illustrate the other cases, they are commented upon in detail.

It will be seen that the amount of acid in solution is in every case in excess of the theoretical. The divergences in Sections B and C increase with the strength of the original solution taken, and the greatest divergence is obtained in Section A, where both acids are present in the solid form. All the differences are far beyond the limits of experimental error.

There are, however, some small corrections to be made in the above figures. The results are given in normalities, whereas to be strictly comparable they should be expressed in gramme-molecules in 100 grm. of water. But this correction, instead of explaining the divergences, only increases them, for, as the solutions become more concentrated, the ratio of the weight of water present to the total weight becomes less, and the correction is thus a positive

* 'Zeits. physikal. Chem.,' 1887, vol. 1, p. 77.

† *Ibid.*, 1903, vol. 46, p. 845.

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Table II.—Salicylic and *o*-Nitrobenzoic Acids.

Initial state.	Acid dissolved (theory).		Acid dissolved (expt.).	Divergences.
A. Solid salicylic	Salicylic = 0·01365 N			
Solid *o*-nitrobenzoic	*o*-Nitrobenzoic = 0·04314 N			
		0·05679 N	0·05843 N	+0·00164 N
B. Known solution salicylic, Solid *o*-nitrobenzoic—				
(*a*) Salicylic = 0·00937 N	*o*-Nitrobenzoic	0·04328 N	0·04357 N	+0·00029 N
(*b*) „ = 0·01356 N		0·04316 N	0·04402 N	+0·00086 N
(*c*) „ = 0·01624 N		0·04301 N	0·04413 N	+0·00112 N
C. Known solution *o*-nitrobenzoic, Solid salicylic—				
(*a*) *o*-Nitrobenzoic = 0·01565 N	Salicylic	0·01430 N	0·01447 N	+0·00017 N
(*b*) „ = 0·04310 N		0·01366 N	0·01445 N	+0·00079 N
(*c*) „ = 0·04358 N		0·01365 N	0·01439 N	+0·00074 N

one, and also increases with concentration. There must also be taken into account the increase of the density of the solution with concentration; this entails a smaller negative correction. The final correction is, therefore, small and positive, in most cases well within the limits of experimental error, and so does not materially affect the results. Density determinations, however, were always made, and in the table below a typical example of the correction is given. Another case is shown after Table III; all other tables give results in normalities only.

Corrections for Density, etc.

The corrections for Section B of Table II are here given. Densities were obtained by means of a 25 c.c. pipette and a weighing bottle, and are liable to an error of 0·0002.

Strength of salicylic acid solution taken.	Density.	Final strength (salicylic and *o*-nitrobenzoic acids).	Density.
—	0·9963	0·04360 N	0·9998
0·00937 N	0·9968	0·05294 N	1·0001
0·01356 N	0·9970	0·05758 N	1·0009
0·01624 N	0·9973	0·06037 N	1·0012

When we express these strengths in gramme-molecules per 100 grm. of water, we obtain the following values. The last column shows the correction necessary to transfer results in normalities to correct results. (For obtaining, however, the "effective" part of this correction, it is necessary to subtract the initial value of it from its value at the given concentration. An example is given below.)

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Strength of salicylic solution.	Total titre.	*o*-Nitrobenzoic dissolved.	Correction.
—	0·04392	0·04392	+0·00032
0·00941	0·05349	0·04399	+0·00042
0·01362	0·05810	0·04448	+0·00046
0·01632	0·06093	0·04461	+0·00048

The "effective" correction is thus, even in the last case, only (0·00048 − 0·00032) = 0·00016. This is less than 0·3 per cent. of the whole titre.

In Sections B and C of Table II it will be seen that not only does the divergence from theory increase with increase of concentration, but that the actual amount of acid dissolved, instead of decreasing, at first rapidly and then more slowly, as demanded by the theory, either shows an increase or becomes practically constant. The divergences from theory are therefore fundamental. The result of another experiment will show this more clearly. A saturated solution of *o*-nitrobenzoic acid, of strength 0·04358 N, free from solid, was added to solid salicylic acid and shaken in the thermostat until constant. The strength was now 0·05797 N. Since the concentration of the hydrogen ion had been increased, the solution should be supersaturated with respect to *o*-nitrobenzoic acid. But on adding solid *o*-nitrobenzoic acid to the solution, and shaking again until the titre was constant, the concentration rose to 0·05845 N, *i.e.* the solution was not supersaturated, but unsaturated.

A comparison of the three results of Sections A, B (*b*), and C (*b*) is interesting. The concentrations of the solutions originally taken in B (*b*) and C (*b*) are, as nearly as possible, those shown by A to be theoretically saturated in presence of the other acid. The final titre should therefore be the same in all three cases. Instead of the theoretical value of 0·05679 N, however, the three values obtained are 0·05843 N, 0·05758 N, and 0·05755 N respectively, which differ widely not only from the theoretical value but also from each other. The presence of solid acid allows an excess beyond theory to be dissolved; this is allowed in the case of both acids in A, in the case of *o*-nitrobenzoic only in B (*b*), and in the case of salicylic only in C (*b*). Hence we may expect the divergence in A to be equal, as a first approximation, to the sum of the divergences in B (*b*) and C (*b*). The experimental results are 0·00164 N and (0·00086 N + 0·00079 N) = 0·00165 N. (See Table II.)

In Sections B (*c*) and C (*c*) saturated solutions (free from solid) of the one acid were taken, and treated with the other solid. Further consideration

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of the results is left over until the remaining experiments on this and other types are given.

The results of other experiments with two weak acids are given in Table III, which shows the solubilities of salicylic and *o*-nitrobenzoic acids in known solutions of formic and malonic acids. In all cases the differences from theory are small and negative, but by making the corrections for density, etc., such differences are either destroyed or converted into small positive divergences, in all cases within error limits of the theoretical result. A typical series of corrections is given in Table IIIA.

Table III.—Remaining Experiments with Two Weak Acids.

Initial state.	Acid dissolved (theory).	Acid dissolved (expt.).	Divergences.
A. Known solutions formic, Solid salicylic—	Salicylic		
(*a*) Formic = 0·05168 N	0·01539 N	0·01531 N	−0·00008 N
(*b*) „ = 0·09977 N	0·01496 N	0·01474 N	−0·00022 N
B. Known solutions formic, Solid *o*-nitrobenzoic—	*o*-Nitrobenzoic		
(*a*) Formic = 0·05168 N	0·04320 N	0·04304 N	−0·00016 N
(*b*) „ = 0·09977 N	0·04289 N	0·04266 N	−0·00023 N
C. Known solutions malonic, Solid salicylic—	Salicylic		
(*a*) Malonic = 0·03126 N	0·01502 N	0·01485 N	−0·00017 N
(*b*) „ = 0·10088 N	0·01417 N	0·01408 N	−0·00009 N
(*c*) „ = 0·20036 N	0·01378 N	0·01362 N	−0·00016 N
D. Known solutions malonic, Solid *o*-nitrobenzoic—	*o*-Nitrobenzoic		
(*a*) Malonic = 0·03126 N	0·04285 N	0·04279 N	−0·00006 N
(*b*) „ = 0·10088 N	0·04159 N	0·04153 N	−0·00006 N
(*c*) „ = 0·20036 N	0·03992 N	0·03967 N	−0·00025 N

Table IIIA.—Corrections for Density, etc.

Known solutions formic acid
Solid salicylic acid
} (see Table III, Section A).

Strength of formic acid solution taken.	Density.	Final strength (formic and salicylic acids).	Density.
—	0·9963	0·01634 N	0·9973
0·05168 N	0·9966	0·06699 N	0·9976
0·09977 N	0·9969	0·11451 N	0·9978

Expressing these strengths in gramme-molecules per 100 grm. water, we have :—

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Strength of formic solution.	Total titre.	Salicylic dissolved.	Correction.
—	0·01642	0·01642	+0·00008
0·05198	0·06745	0·01547	+0·00016
0·10054	0·11553	0·01499	+0·00025

The "effective" correction is only (0·00025−0·00008) = 0·00017 at the greatest concentration. This is less than 0·2 per cent. of the whole titre.

In the next table there are given the results of experiments with two strong acids. For the calculation of the theoretical results the following table of dissociation values for hydrochloric acid was used:—

v =	16	32	64	128,
m =	0·935	0·953	0·966	0·972.

The dissociation values of picric and methyl picric acids at various dilutions have already been given.

Table IV.—Experiments with Two Strong Acids.

Initial state.	Acid dissolved (theory).	Acid dissolved (expt.).	Divergences.
A. Known solutions hydrochloric, Solid methyl picric—	Methyl picric		
(*a*) Hydrochloric = 0·00895 N	0·00669 N	0·00641 N	−0·00028 N
(*b*) „ = 0·01593 N	0·00510 N	0·00487 N	−0·00023 N
B. Known solution picric acid, Solid methyl picric—	Methyl picric		
(*a*) Picric acid = 0·01013 N	0·00651 N	0·00702 N	+0·00051 N

Here also divergences from theoretical results are obtained; negative in the case of methyl picric and hydrochloric, positive in the case of methyl picric and picric acids.

Table V gives examples of weak acids (salicylic and *o*-nitrobenzoic) dissolved in known solutions of a strong acid (hydrochloric). The divergences are pronounced, and in the negative direction. In the example A (*b*) it will be seen that the decrease is large enough, although the hydrochloric acid solution is only one-thirtieth normal (rather more than a gramme per litre), to bring the total amount of salicylic acid dissolved below its "constant undissociated value." A corresponding result was obtained by Arrhenius (*loc. cit.*) only with more concentrated solutions of two strong electrolytes.

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Table V.—Weak Acids in Hydrochloric Acid Solutions.

Initial state.	Acid dissolved (theory).	Acid dissolved (expt.).	Divergences.
A. Known solutions hydrochloric, Solid salicylic acid—	Salicylic		
(*a*) Hydrochloric = 0·01786 N	0·01345 N	0·01290 N	−0·00055 N
(*b*) „ = 0·03573 N	0·01310 N	0·01238 N	−0·00072 N
B. Known solutions hydrochloric, Solid *o*-nitrobenzoic acid—	*o*-Nitrobenzoic		
(*a*) Hydrochloric = 0·01786 N	0·03753 N	0·03681 N	−0·00072 N
(*b*) „ = 0·03573 N	0·03478 N	0·03390 N	−0·00088 N

Table VI below completes the series by giving those cases in which a strong acid (methyl picric) was dissolved in known solutions of weak acids (salicylic and *o*-nitrobenzoic). In the case of methyl picric and salicylic acids a full investigation was made, similar to that carried out with salicylic and *o*-nitrobenzoic acids.

Table VI.—Methyl Picric Acid and Weak Acids.

Initial state.	Acid dissolved (theory).		Acid dissolved (expt.).	Divergences.
A. Known solution *o*-nitrobenzoic, Solid methyl picric acid—				
(*a*) *o*-nitrobenzoic = 0·01975 N	Methyl picric	0·00736 N	0·00800 N	+0·00066 N
B. Solid salicylic acid	Salicylic = 0·01404 N			
Solid methyl picric acid	Methyl picric = 0·00935 N			
		0·02339 N	0·02613 N	+0·00274 N
C. Known solutions salicylic acid, Solid methyl picric acid—				
(*a*) Salicylic = 0·00981 N	Methyl picric	0·00955 N	0·01063 N	+0·00108 N
(*b*) „ = 0·01393 N		0·00935 N	0·01072 N	+0·00137 N
D. Known solution methyl picric, Solid salicylic acid—				
(*a*) Methyl picric = 0·00938 N	Salicylic	0·01404 N	0·01532 N	+0·00128 N

The results of sections B, C (*b*), and D may be compared. In the two latter the strengths of the original solutions are those shown by B to be theoretically saturated in presence of the other acid. (Compare Table II.) The divergence in B may be expected to be equal to the sum of the other two divergences, to a first approximation. The experimental results are 0·00274 N and (0·00137 N + 0·00128 N) = 0·00265 N.

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The differences in Table VI are all large and positive. It will be seen that methyl picric acid is more soluble in salicylic acid solutions than in pure water.

In none of the above tables is the theory exactly followed, and a further experiment was performed, to ascertain whether the divergences obtained were superposable. A known solution of hydrochloric acid was taken, and two weak acids (salicylic and *o*-nitrobenzoic acids) added. The differences to be expected from theory were estimated by interpolation from the results of the preceding tables, and compared with the difference experimentally obtained.

Table VII.—Two Weak Acids in Hydrochloric Acid Solution.

Initial state.	Acid dissolved (theory).	Acid dissolved (expt.).	Divergence.
Known hydrochloric acid solution, Solid salicylic acid, „ *o*-nitrobenzoic acid—	Salicylic = 0·01316 N *o*-Nitrobenzoic = 0·03608 N		
(*a*) Hydrochloric = 0·02957 N...	0·04924 N	0·04935 N	+0·00011 N

The following divergences were to be expected (see Tables II and V):—

(*a*) Due to solid salicylic and solution of *o*-nitrobenzoic +0·0006 N.
(*b*) Due to solid *o*-nitrobenzoic and solution of salicylic +0·0008 N.
(*c*) Due to solid salicylic and solution of hydrochloric −0·0006 N.
(*d*) Due to solid *o*-nitrobenzoic and solution of hydrochloric −0·0008 N.

The solution should therefore be approximately of theoretical strength if the various differences are superposable. Seeing that the accuracy of a large number of experiments is involved in the values of the expected divergences given above, the experimental result agrees with this supposition well within the limits of error.

A general consideration of the results in Tables II to VII shows that the theory holds strictly in none of the possible combinations of acids. It makes no difference whether they are both weak, both strong, or one of each type; similar divergences of several per cent. are obtained in every case. And these divergences, though usually numerically small, are fundamental in each direction; the upper limit consistent with the theory—the total solubility in pure water—and the lower limit—the "constant undissociated value"—are both passed in very dilute solutions.

Now, on an examination of the tables, the following rule appears to hold:

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that an increase beyond theoretical is obtained when two acids chemically similar (*i.e.*, salicylic and *o*-nitrobenzoic) are present in solution, and a decrease when two acids chemically dissimilar (*i.e.*, salicylic and hydrochloric) are present. This rule seems to be quite general, and not dependent at all upon the types of the two acids. In Table III the two acids are of neither very similar nor very dissimilar character, and the divergences obtained are but slight, and within error limits of the theoretical. There may be an increase or a decrease, but, at the concentrations tested, it is too small a percentage of the total titre to be perceived.

The fact that a solution of one acid can dissolve more of a chemically similar acid than theory demands, leads to the inquiry whether the ionic effect of the acids upon each other is not also accompanied by a solvent effect. The small quantity of the first acid in solution might, by its solvent action upon the second acid, cause an appreciable increase in the result. That the cause is quite adequate may be seen from the relatively large increase in the solubility of methyl picric acid in water in the presence of small quantities of ligroin or benzene dissolved in the water, as before described. A decrease below the theoretical result would be accounted for, under this view, by the comparative insolubility of the two acids in each other.

The divergence from theory would thus steadily increase with increase of concentration, and this is actually the case. Stronger confirmation, however, is given to the hypothesis by the results of the two series of experiments carried out with salicylic and *o*-nitrobenzoic acids, and with salicylic and methyl picric acids, respectively. When both acids are present in the solid form, both exert a solvent effect, and this is, to a first approximation, found to be the sum of their two separate solvent effects, determined by suppressing the solid form of one acid, and having it present instead as a solution, theoretically saturated in the presence of the other acid.

To test the above view further it is necessary to perform a series of experiments with one solid and one liquid acid, the solubility of the solid acid in the liquid one being either much greater or much less than its solubility in pure water. From the solubility results obtained by treating the solid acid with known solutions of the liquid acid in water it can then be seen whether the increase or decrease from theory is capable of being accounted for in this way.

The case of salicylic or *o*-nitrobenzoic with formic acid is a good example, both solids being much more soluble in formic acid than in water. The above, however, were the only cases in which no definite increase or decrease from theoretical was observed, the error limit obscuring the result at the concentrations tested.

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Another series of experiments was therefore carried out with more concentrated solutions, both in the above and in other cases. The method of estimating volumetrically with baryta here became impracticable, owing to the overwhelming concentration of the solvent acid compared with that of the acid dissolved, in which latter small variations were consequently impossible to measure.

The method employed was that of evaporation. The solutions were prepared in the same manner as already described, 25 c.c. of the liquid were pipetted out into a weighed evaporating dish, and evaporated down to dryness. The amount of the dissolved solid was then found by weighing, and its titre in the solution directly calculated. The cases investigated were :—

(*a*) In solutions of formic acid : Salicylic acid, hippuric acid.
(*b*) In solutions of acetic acid : Salicylic acid.
(*c*) In solutions of hydrochloric : Salicylic acid, *o*-nitrobenzoic acid.

Solutions containing hippuric acid could be evaporated down on the steam-bath without loss of solid by volatilisation; those containing salicylic and *o*-nitrobenzoic acids, since these proved to be more or less volatile with steam, were allowed to evaporate slowly at the ordinary temperature.

The residues obtained weighed from 0·1 to 0·04 of a gramme; the error limit in the latter case is about 1 per cent. Experiments performed in duplicate gave results agreeing together within this limit, and the results of this method, as tested with some of the more dilute solutions, were closely concordant with those obtained volumetrically.

The results obtained are shown in both tabular and graphic form. Some volumetric determinations are also given in the tables, both for the purpose of comparison with the gravimetric results and for use in the accompanying curves.

Results are expressed, as before, in normalities. The corrections described in the volumetric determinations, although much larger here owing to the greater concentrations of the solutions used, are not applied. That due to density change is never so much as 1 per cent. of the total, and is therefore still within the limits of experimental error. That due to replacement of water by acid is as much as 10 per cent. of the total in the most concentrated solutions, but since we are here considering the solvent actions of both water and acid, it is preferable to compare solutions containing equal weights of total solvent than those containing equal weights of water, and such solutions are represented, within error limits, in the uncorrected figures below.

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Table VIII.—Gravimetric Determinations.

A. Salicylic Acid in Solutions of Formic Acid. (See fig., p. 216.)

Strength of formic acid solution (per cent.).	Weight of residue from 25 c.c. (in grms.).	Strength of dissolved acid (gravimetrically).	Strength of dissolved acid (volumetrically).
0	0·0563	0·01631 N	0·01634 N
0·24	—	—	0·01531 N
0·46	—	—	0·01474 N
0·625	0·0512	0·01484 N	—
1·25	0·0516	0·01496 N	—
2·5	0·0530	0·01536 N	—
5	0·0592	0·01716 N	—
10	0·0725	0·02101 N	—

B. Hippuric Acid in Solutions of Formic Acid. (See fig.)

Strength of formic acid solution (per cent.).	Weight of residue from 25 c.c. (in grms.).	Strength of dissolved acid (gravimetrically).	Strength of dissolved acid (volumetrically).
0	0·0915	0·02045 N	0·02048 N
1·25	0·0901	0·02014 N	—
2·5	0·0930	0·02078 N	—
5	0·1018	0·02275 N	—
10	0·1191	0·02661 N	—

C. Salicylic Acid in Solutions of Acetic Acid. (See fig.)

Strength of acetic acid solution (per cent.).	Weight of residue from 25 c.c. (in grms.).	Strength of acid dissolved (gravimetrically).
0	0·0563	0·01631 N
0·625	0·0584	0·01691 N
1·25	0·0602	0·01745 N
2·5	0·0636	0·01846 N
5	0·0710	0·02059 N

D. Salicylic Acid in Solutions of Hydrochloric Acid. (See fig.)

Strength of hydrochloric acid solution.	Weight of residue from 25 c.c. (in grms.).	Strength of dissolved acid (gravimetrically).	Strength of dissolved acid (volumetrically).
—	0·0563	0·01631 N	0·01634 N
0·0179 N	—	—	0·01290 N
0·0357 N	—	—	0·01238 N
0·125 N	0·0419	0·01214 N	—
0·25 N	0·0412	0·01194 N	—
0·5 N	0·0387	0·01123 N	—

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E. *o*-Nitrobenzoic Acid in Solutions of Hydrochloric Acid. (See fig.)

Strength of hydrochloric acid solution.	Weight of residue from 25 c.c. (in grms.).	Strength of dissolved acid (gravimetrically).	Strength of dissolved acid (volumetrically).
—	0·1804	0·04320 N	0·04360 N
0·0179 N	—	—	0·03681 N
0·0357 N	—	—	0·03390 N
0·125 N	0·1245	0·02980 N	—
0·25 N	0·1221	0·02922 N	—
0·5 N	0·1188	0·02846 N	—

The solubility curves obtained from the above table, as shown in the diagrams, consist of three types, according to the acid used as solvent. With solutions of acetic acid there is a continuous and regular increase in the solubility, with hydrochloric solutions a sharp initial decrease is obtained, followed by a much smaller and more regular decrease, while with formic acid solutions a small initial decrease is with increasing concentration soon converted into a regular increase.

The first case, that of acetic acid, may be considered as a case of pure solvent effect, for the degree of ionisation of the acid is so small that the ionic concentration could have, even in concentrated solutions, no measurable effect. The increase in solubility is proportional to the concentration of the acid in solution, and is quite regular as water is replaced in the solution by more solvent acid.

Formic acid is comparatively much stronger than acetic, and here it appears that the ionisation effect upon the acids employed is at first the more important, but the decrease in the solubility thus produced is soon neutralised, as the concentration increases, by the greater solvent power of the formic acid. The curve finally approximates to a straight line corresponding to the acetic acid type, showing a regular increase with increase of concentration. Thus there are two separate influences upon the solubility; an ionic effect proportionally large at first, but rapidly falling off with increase of concentration, and a solvent effect, directly proportional to the concentration.

With hydrochloric acid solutions the ionic effect is again considerably stronger than in the former case, and the solvent effect is negligible. A sharp drop, as the strength of the hydrochloric increases, carries the solubility of the acids used below the "constant undissociated value," and further decrease is very slow, being presumably due to the replacement of solvent water by non-solvent acid in the solution. In this case also the curve finally approximates to a straight line.

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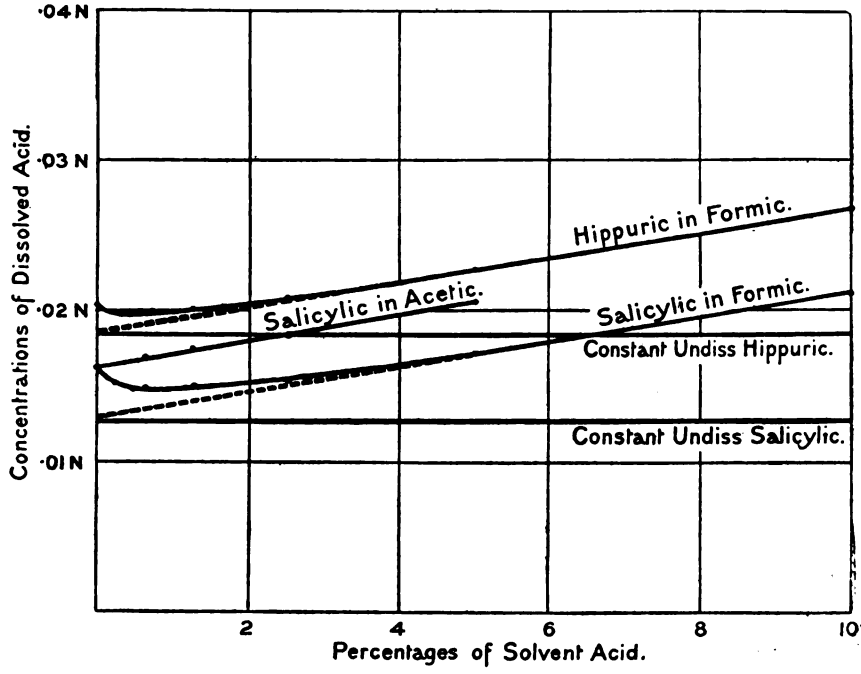

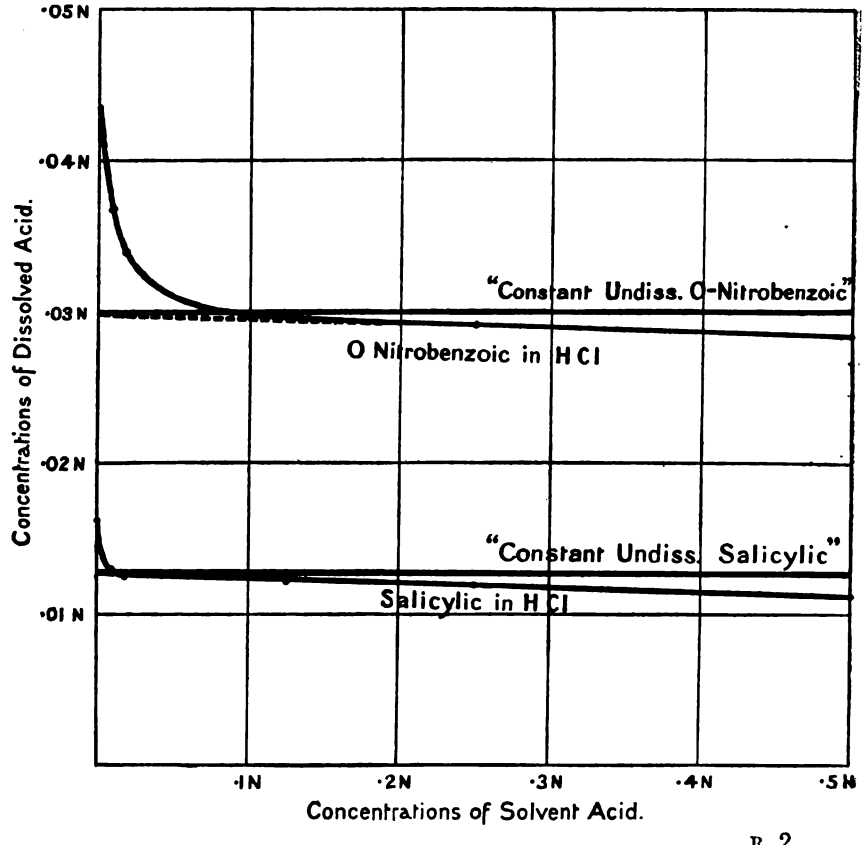

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If these straight lines are produced backwards to meet the axis, it will be seen that they do so at or near the point of the so-called "constant undissociated value." (The only exception is in the case of salicylic in acetic acid, but this is practically a case of pure solubility.) Thus, if we consider these lines as dividing lines, we may regard the solubility of one acid in aqueous solutions of another as consisting of two portions:—

(*a*) An undissociated portion (below the line), increasing or decreasing regularly, according as the acid is more or less soluble in the solvent acid than in water.

(*b*) A dissociated portion (above the line), decreasing more or less rapidly according to the ionic strength of the solvent acid. This decrease is not regular, but is proportionally greater the less concentrated the solution is, falling off as the dissociated portion is suppressed by increase of concentration.

The solvent effect, acting directly upon the undissociated portion, will also indirectly affect the dissociated part of the substance in solution, since this must remain in equilibrium with the undissociated part. In the curves given, the acids exist in solution mainly in the undissociated state, hence this indirect effect is but small, and soon becomes negligible with increase of concentration, owing to the almost total suppression of the ionised part. In solutions of strong electrolytes, however, the indirect may be greater than the direct effect; hence the solubility curves in such cases will not finally approximate to straight lines which cut the axis, when produced backwards, at or very near to the "constant undissociated value." The case of salicylic acid in solutions of acetic acid is another example of the inapplicability of the rule in the event of the ionised portion persisting in appreciable quantity at all concentrations of the solvent acid.

The experimental divergences obtained from the values indicated by the theory of the constant solubility-product can thus be accounted for in all cases by this solvent effect. The divergences, positive or negative, are caused by the solvent influence of the two substances upon each other, and this, as shown in the above tables, is positive when the substances are chemically similar in character, negative when they are dissimilar. The amount of the divergence due to each acid can also, as in the case of salicylic and *o*-nitrobenzoic acids, be obtained to a first approximation.

The existence of this solvent effect renders it evident that the reverse problem, attempted by Noyes, of calculating the degree of dissociation of one substance by determining its solubilities in water and in a known solution of another substance containing a common ion, may sometimes lead to very erroneous results. In any case the results of such a

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determination must be uncertain, since a wide variation in the assumed degree of dissociation corresponds in most instances to a very small change in the solubility, any decrease in undissociated substance dissolved being almost entirely balanced by an increase in dissociated, and *vice versâ*. This fact explains also why, although the degrees of dissociation of the strong acids used in the above research are not yet accurately determined, being liable to an uncertainty of several per cent. in dilute solutions, the solubility results of other acids with them, as calculated from these values, are subject to a much smaller degree of error.

In conclusion, I have much pleasure in expressing my thanks to Prof. Walker, at whose suggestion and under whose direction the above research was carried out, for his advice and assistance during the whole period of its execution.

Bakerian Lecture.—*A Chemically Active Modification of Nitrogen, Produced by the Electric Discharge.*

By the Hon. R. J. Strutt, F.R.S., Professor of Physics, Imperial College of Science, South Kensington.

(Received March 16,—Lecture delivered April 6, 1911.)

[Plate 8.]

§ 1. *Afterglow of Nitrogen.*

It is known that vacuum tubes frequently show a luminosity of the contained gas after discharge is over. In a previous paper* I was able to show that this effect, as it occurs in air, is of the nature of a phosphorescent combustion, and is due to the mutual reaction of nitric oxide and ozone, each formed in the discharge. In a second paper† it was shown that other phosphorescent combustions can be observed in ozone, notably of sulphur, sulphuretted hydrogen, acetylene, and iodine. Some of these give continuous spectra, but the majority band spectra.

In the first paper it was stated that pure nitrogen gives no afterglow whatever, and, with the simple induction coil discharge with which I was then working, this has been frequently verified since. Mr. Percival Lewis has however, described an afterglow obtained in nitrogen when a jar

* 'Phys. Soc. Proc.,' Dec. 15, 1910, vol. 23, p. 66.
† *Ibid.*, Feb. 15, 1911, vol. 23, p. 147.

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discharge with spark-gap is used.* I had no difficulty in obtaining this glow as soon as the jar discharge was used, and have applied to its examination the method used in the former papers. This is due to Sir James Dewar,† and consists in drawing a current of gas through the vacuum tube into an observing vessel, where the glow is developed, and thence into an air pump, which must be a mechanical one of good construction, driven by power. It is thus possible to examine the properties of the glowing nitrogen much more satisfactorily than can be done by intermittent examination after successive discharges.

As Lewis observed, the glow has a characteristic band spectrum not known in any other connection. Its most conspicuous features in the visual region are a green, a yellow, and a red band, of not very unequal intensity. The yellow one is usually the brightest, and imparts a yellow colour to the glow, not very dissimilar to that of the afterglow in air, due to the union of nitric oxide and ozone. The two glows are, however, instantly distinguished by the spectroscope, the air glow giving a continuous spectrum. I have obtained the nitrogen afterglow intense enough to be conspicuous to an observer 30 feet off, when it was 18 inches below a 32-candle electric lamp.

With regard to the conditions for its production, my observations do not altogether agree with those of Lewis. He obtained it with nitrogen from sodium nitrite and ammonium chloride, but was unable to do so from atmospheric nitrogen. He was disposed to regard the presence of a trace of nitric oxide as necessary. I obtained it first from air which had passed over red-hot copper, and afterwards from air which had been freed from oxygen in the wet way by Hempel's copper and ammonia method.‡

It has been shown by Von Mosengeil§ that nitrogen completely freed from oxygen by sodium can give the afterglow. I have confirmed this by bubbling atmospheric nitrogen through melted phosphorus, and thence into the vacuum tube. The glow seemed rather improved than otherwise by this treatment. No luminosity was observed in the phosphorus.

Nitrogen prepared by burning phosphorus in air under a large bell-jar gives the glow, but not well. It is not free enough from oxygen. In short, all the evidence obtained points to the conclusion that the glow is connected with nitrogen, and nothing but nitrogen.

For experiments on the glow, particularly if they are to be prolonged, it is

* 'Ann. d. Phys.,' 1900, vol. 2, p. 466; 'Phys. Zeit.,' 1904, vol. 5, p. 546.

† 'Roy. Inst. Proc.,' 1888, and 'Engineering,' June 18, 1909.

‡ It is necessary to remove carbon dioxide and ammonia by appropriate absorbents when using this method, or the glow fails. Special drying of the nitrogen, on the other hand, seems to be of no advantage.

§ 'Ann. d. Phys.,' 1906, vol. 20, p. 833.

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convenient to make use of commercial cylinders of compressed nitrogen, provided with the usual automatic regulators as used in connection with the limelight. Commercial nitrogen is not free enough from oxygen for immediate use, but it can readily be made so by passage through a tube filled with freshly cut or cast fragments of phosphorus. A glow is seen where the nitrogen enters, indicating that an absorption of residual oxygen is in progress. This only extends a short way down the tube, and the darkness of the remainder is a guarantee that absorption is complete, and that the issuing nitrogen is fit for use. The phosphorus tube should not be unnecessarily exposed to daylight, as this causes deterioration of the absorbent surface.

§ 2. *Effect of Temperature.*

If a long tube, through which a stream of glowing nitrogen passes, is moderately heated, the glow is locally extinguished. As the gas passes on to a cooler part of the tube its luminosity is recovered. If, on the other hand, the gas is led through a tube immersed in liquid air, it glows out with increased brilliancy where it approaches the liquid air. The luminosity is completely and finally extinguished when, or before, the fully cooled portion of the tube is reached. This increased brilliancy is obviously the counterpart of the temporary obscurity observed with heat. Whatever the atomic or molecular change may be, of which the afterglow is a sign, these experiments show that it is accelerated by cooling, and retarded by heating. The kind of change which may be expected to behave in this way is an association, *e.g.* of dissociated nitrogen atoms into molecular nitrogen.

It may be doubted, however, whether the visual glow is a perfect measure of the changes in progress. I find that if a tube carrying the glow is strongly heated the glow is permanently extinguished. It is clear that the view suggested above is incomplete.

§ 3. *Effect of an Electric Field.*

The question will naturally present itself whether the gaseous ions of the discharge, which no doubt remain in the glowing nitrogen, have any direct connection with its peculiarities. If this were the case, we should expect that by passing the glowing gas through an electric field so as to remove the ions, the glow, and its power of exciting metallic spectra, to to be presently described, would be destroyed. Glowing nitrogen was passed down a tube about 40 cm. long and 2 cm. in diameter, provided internally with tin-foil strips along the whole length on the opposite sides. The glow was in no way affected at any part of the tube, if an E.M.F.

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of 200 volts was applied to these strips. Nor was its power of exciting the spectrum of some sodium vapour at the further end at all diminished (see below, § 5).

§ 4. *Action of the After-glowing Nitrogen on the Non-metals.*

The glowing nitrogen has remarkable chemical properties.

Drawing it by the pump over a small pellet of phosphorus a violent reaction occurs, red phosphorus is formed,* and the yellow glow is quenched. At the same time the gas is absorbed. This latter experiment can readily be shown by means of a tube illustrated in fig. 1. The tube is in this case closed, and has no current of nitrogen through it. The discharge passes between the electrodes A and B as indicated by the dotted line. The afterglow diffuses into the annex C, where its characteristic colour and spectrum may be seen. On the other hand, phosphorus vapour diffuses out from the pellet of that substance at D, and they meet at a point E, where the reaction occurs, and red phosphorus is deposited as a film along the walls of the tube. The changed appearance of the discharge shows that absorption is in progress. Beginning with enough nitrogen to give a threadlike discharge, in a few minutes the pressure is sufficiently reduced to broaden out the discharge so as to fill the tube. Shortly after that the vacuum becomes quite high, and conduction ceases.

Returning to the experiment where a continuous stream of nitrogen is maintained by the pump, it is found that if the Leyden jar is suppressed, and the ordinary coil discharge employed, a piece of phosphorus in the stream of nitrogen is very little acted on. There is just perceptible action in a few minutes, and a faint greenish flame may be seen round the phosphorus. The same flame may be seen more conspicuously with the jar discharge, but only for a moment; for it is almost immediately obscured in this case by the opaque deposit of red phosphorus on the walls of the tube.

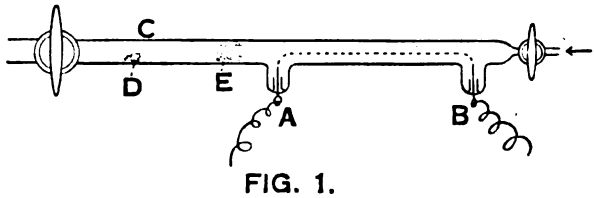

FIG. 1.

No doubt the ordinary coil discharge has the same kind of effect as the jar discharge, but in a degree too slight to make the afterglow visible, and only apparent by prolonged action on phosphorus.

* Other cases are known where the reaction of phosphorus with another body converts the excess into red phosphorus. Iodine behaves thus.

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The novelty of these observations lies in the fact that the phosphorus vapour employed has no access to the region of discharge. It has long been known that phosphorus vapour in the region of discharge would combine with nitrogen, and the fact has been made use of since 1893 in the exhaustion of incandescent lamps.* Discharge takes place through the rarefied air between the ends of the filament. The E.M.F. of, say, 100 volts between these is amply sufficient to produce it with a white-hot cathode.

Sir Oliver Lodge, too, has used phosphorus in exhausting his vacuum valves.† No one, however, seems to have suspected that nitrogen could continue to react with phosphorus after it had left the discharge, and even after it had been deprived of ions by passing through an electric field. Nor has the reaction been connected with the afterglow.

I have made use of the reaction with phosphorus to determine what percentage of active nitrogen is present in the gas shortly after leaving the discharge tube. The principle of the method is to determine the gain in weight of the phosphorus after a measured volume of nitrogen has been passed over it.

Fig. 2 shows the apparatus. Active nitrogen enters from a vacuum tube attached by a short indiarubber connector to the stopcock A. It passes over fragments of phosphorus at B, where it is absorbed with deposition of red phosphorus, and the glow disappears. The gas then passes through a U-tube C, cooled in liquid air. This is to prevent any phosphorus vapour being carried off. Finally, the gas leaves through a stopcock D. The entire arrangement can be detached and hung on the balance by the wire loop E. The phosphorus is originally introduced through F, which is then sealed. The weighings were always carried out with the tube vacuous, and every precaution was taken against the entrance of moisture, which might lead to erroneous results.

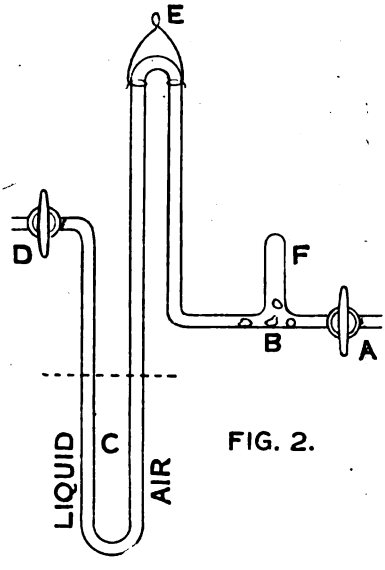

FIG. 2.

In a typical experiment 2540 c.c. of nitrogen were passed, and the gain in weight was 15·5 mgrms. Thus the nitrogen absorbed was 12·2 c.c.,

* See, for instance, J. Rodet, 'Lampes à Incandescence,' p. 107, Paris, Gauthier-Villars, 1907.

† Patent No. 25047, 1905.

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1/210 part of the whole. It appears that the percentage of nitrogen converted into the active form is comparable with the percentage of oxygen converted in an ozoniser.

The glowing nitrogen also exhibits remarkable phenomena when led over iodine. Its normal yellow glow is replaced by a magnificent light blue flame, at the place where it mingles with the iodine vapour. The appearance is represented in the coloured plate. A slight rise of temperature is observed where the blue glow originates. The iodine is quite volatile enough without the application of heat. I have not succeeded in demonstrating the absorption of nitrogen in this case, nor have I been able to see any signs of a compound deposited further on in the tube. It may be masked by the excess of iodine.

The flame gives a magnificent spectrum of broad bands. Details will follow in a later paper. Brief notes will now be given on the behaviour of a few other non-metallic elements.

Sulphur, when warmed in the current of glowing nitrogen, extinguished it; and, with somewhat stronger heating, a blue flame or glow was apparent, though not comparable in volume or intensity with that of iodine. A transparent green deposit is formed on the glass.

Selenium had no effect.

Arsenic, heated in the glow, gave a not very conspicuous green flame, with a spectrum which seemed continuous, or, at all events, lacking in conspicuous features, and extended over the whole visual region.

Antimony and *carbon* gave no effect.

When *hydrogen* is admitted to mix with the glowing nitrogen, after the latter has been through the vacuum tube, no effect is produced, beyond a mere dilution of the glow.

Oxygen, on the other hand, destroys the glow without any other luminosity being developed in the process.

§ 5. *Action on the Metals—Production of Metallic Line Spectra.*

When the glowing nitrogen is led over a fragment of sodium, which is heated a little above its melting point, the sodium spectrum is developed with great brilliancy. Indeed, the power of developing the D line is a more sensitive test for the presence of the active nitrogen than any other.

When the sodium is more strongly heated, say, to 250° C., a curious effect is observed. The denser vapour in the immediate neighbourhood of the metal becomes visually green, showing the green line E very strongly, while the D line is scarcely visible. On either side of the central green light is an outer luminous region in which the D line predominates.

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I have been able to observe the absorption of the glowing nitrogen by sodium, by the same method as was employed with phosphorus. The sodium vapour was not allowed to penetrate into the discharge, and its spectrum was not observed there.*

There seems to be no reason for doubting that the sodium spectrum seen in these experiments is simply the flame spectrum of sodium burning spontaneously in the active nitrogen, to form the nitride. It opens up a new field of experiment to be able to produce metallic spectra in a vessel at so low an average temperature, and in the absence of an electric field. The line spectra of many other metals have been obtained similarly. The following have been observed:—Cadmium, magnesium, mercury, potassium, zinc, lead. Thallium was tried in the form of chloride, and gave a magnificent green light, in striking contrast to the yellow afterglow which it replaces.

The sodium spectrum, too, can be obtained when the glow passes through a soda glass tube, heated to near the softening point, but in this case the D line alone appears.

In the case of metallic mercury, absorption of nitrogen was proved, as with sodium and phosphorus, though, working in a closed vessel without a current of gas, it was not found feasible in practice to prevent mercury vapour finding its way into the discharge. There is no doubt that this is the action described by Threlfall.† He observed the absorption of nitrogen when a jar discharge was passed through it at a low pressure in presence of mercury, though there is no reference to the afterglow in his paper. He observed, too, the formation of a compound which decomposed with a slight explosion when moderately heated.

Although in the absorption experiments mercury could not be prevented from getting into the discharge, it was easy to avoid this when the air pump was used, and a continuous current of nitrogen drawn through. Working thus, I have observed that Threlfall's explosive nitride is formed when the mercury spectrum is developed by the afterglow. This seems conclusive evidence that the production of these spectra is a direct result of the chemical union of the metal with the active nitrogen.

It may be remarked that, though the hot metals (*e.g.*, zinc) are rapidly skinned over with nitride, cold metals remain bright in the nitrogen glow. This was tried particularly with sodium, and with mercury—the latter in the form of a bright film on a copper plate. The clean cold metals have no unfavourable influence on the luminosity of the glow itself.

* This distinguishes the present action from the well-known absorbing power of the alkali metals when used as cathode in a discharge.

† 'Phil. Mag.,' Jan., 1893, p. 1.

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§ 6. *Action on Compound Bodies.*

Some gases and vapours mixed with the glow merely dilute it. Water and carbon dioxide are examples.

In one case an obvious chemical attack has been observed. This was with naphthalene, which turns brown, a brown deposit forming also in the walls of the tube where the nitrogen is passed over it. The nitrogen glow was destroyed, but no luminous phenomena accompanied the action. Heat was not applied.

Ammonia was another case where the original glow was destroyed without attendant luminous effects. It seems likely that a chemical action occurs here, but proof has not been obtained.

It is certain, however, that in some cases destruction of the glow by contact with another substance may occur without chemical action. Manganese dioxide and copper oxide are at once fatal to it. The analogy to the known destruction of ozone by these substances cannot fail to attract attention.

A small roll of superficially oxidised copper gauze was placed in a glass tube and carefully weighed. It was then inserted between the vacuum tube and the pump by means of indiarubber connectors, and a stream of the glowing nitrogen passed over it for about half an hour. The glow abruptly stopped at the surface of the copper oxide. The tube was detached and reweighed. No change of weight amounting to 1/10 mgrm. could be detected, though the quantity of active nitrogen passed, judged by the phosphorus experiments described above, must have amounted to several milligrammes. I conclude that the glow is destroyed in these cases by a catalytic action.

Another class of compound substances become luminous with characteristic band spectra when vaporised in the glow. Stannous and stannic chloride both give the same brilliant and voluminous blue glow. Most of the light comes from one broad symmetrical band in the blue and violet regions. There are, in addition, a number of lines in the ultra-violet, chiefly due to tin. Mercuric iodide gives a violet glow with a strong unsymmetrical violet band distinct from any in the iodine afterglow spectrum mentioned in § 4. Distinctive glows have also been obtained from other mercury salts. Mercurous chloride gives a green one.

Cuprous chloride gives a blue-green glow, with a spectrum agreeing with that shown by the same compound in the Bunsen flame, but with additional features not present in the latter.

Cyanogen gas fed into the glow gives the lilac flame of cyanogen with its well-known spectrum.

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The band spectrum of iodine in the afterglow (see § 4) should probably be regarded as of similar origin with these compound spectra. They are I think, essentially flame spectra, as are also the line spectra of metals produced in the afterglow; but the afterglow must be regarded as a much more searching kind of flame than the ordinary high-temperature flames.

In much of the literature of flame spectra it is implied that temperature is a measure of the spectrum-developing quality of a flame, and no doubt the fact that the oxy-acetylene and oxy-hydrogen flames are, each in its own degree, capable of developing more lines than the Bunsen flame, is favourable to this view. Yet the balance of evidence is greatly against the idea that heat alone is capable of exciting line and band spectra at all; and if we reject this idea it is evidently unreasonable to assume that temperature alone governs the number of lines or bands emitted.

Regarding, then, the afterglow as a flame capable of developing spectra, we have the means of examining the spectra of a number of compounds which will not endure the temperature of an ordinary flame without decomposition. Moreover, the spectrum is better developed. Cuprous chloride, which gives a characteristic spectrum in the Bunsen flame, gives the same spectrum, with additional details, in the afterglow. Compounds like mercuric iodide, instantly decomposed in the Bunsen flame, give in the glow a spectrum not before recognised. It may be possible to obtain valuable generalisations from the examination of a long series of such spectra.

Nitric oxide, allowed to mix with the active nitrogen, shows a very strange behaviour. A greenish flame, possessing a continuous spectrum, is produced, and heat is developed at the point of confluence. To test whether any gas condensable at $-180°$ was produced, the gases from the flame were led through a U-tube cooled in liquid air, and a dark blue substance was condensed out. This melted to an indigo-blue liquid, and finally revealed itself as nitrogen peroxide by evaporating off into an orange gas, soluble in caustic alkali.

It is very surprising that a reaction between nitrogen and nitric oxide should lead to the formation of a substance, not *less*, but *more* oxidised than the latter.

A critic may naturally object that the formation of nitrogen peroxide may have been due to oxygen which accidentally gained admission to the nitric oxide, quite independently of the active nitrogen. I wish to emphasise a test experiment, which disproves this hypothesis.

The influence of the active nitrogen may be removed by simply turning off the electric discharge. The apparatus being in adjustment, with a suitably regulated flow of the gases, the U-tube was kept cool with liquid air for

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10 minutes, after which the liquid air was removed, and the tube allowed to warm up somewhat, for the removal of hoar frost from the outside. No trace of the indigo liquid could be seen. Now the discharge was started, and the tube kept in liquid air for only two minutes. At the end of this time the indigo liquid was extremely conspicuous. The tube could be warmed up to allow the stream of gases to wash out the product, and the experiment could be repeated, on and off, as often as desired. The supply of gas, adjustment of taps, etc., were left absolutely untouched throughout.

It would seem that the reaction which occurs may be of this kind:—

$$2NO + N = NO_2 + N_2.$$

However, I lay no stress on this. I wish only to insist on the definite facts above stated.

Brilliant glows are obtained from some carbon compounds containing the halogens, for instance, a lilac glow from ethyl iodide. This, examined spectroscopically, shows a magnificent cyanogen spectrum. The fact is evidence that the active nitrogen attacks the carbon compound, combining with the carbon; iodine is set free, and may be collected as a conspicuous sublimate by cooling the resulting vapours in liquid air. What becomes of the hydrogen has not yet been determined.

Chloroform and carbon tetrachloride also give a fine cyanogen spectrum. In this case the glow is visually orange, owing to greater relative intensity in the red portion of the cyanogen spectrum. Chlorine is set free, and can be collected in liquid air.

Again, the lilac cyanogen glow is obtained when acetylene is fed in. The experiment mentioned above, where cyanogen itself is shown to give this glow under the same conditions, suggests very strongly that in all these cases the active nitrogen attacks the carbon compound, forming cyanogen, which is merely stimulated, without further change, by the peculiar conditions existing in the glow.

The formation of cyanogen was proved more directly as follows:—The gases from the acetylene experiment were condensed by liquid air, and afterwards collected through a Toepler pump. They were agitated with caustic potash solution to absorb any cyanogen present from the excess of acetylene. The presence of a cyanide in this solution was readily proved by abundant formation of Prussian blue, and by the ferric sulphocyanate reaction. It should be mentioned that, in addition to the condensed gases, some black tarry substance was present in the tube.

Finally, the cyanogen spectrum has been observed when the active nitrogen is allowed to react with methane, pentane, ethylene, alcohol, ether, and

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benzol. It is not, however, so conspicuous in these cases, and probably does not indicate the main course of the reaction.

§ 7. *Summary and Conclusion.*

The leading facts established are:—

(1) That pure nitrogen, from whatever source, subjected to the jar discharge, undergoes some modification which causes it to glow for a short time after it has left the discharge.

(2) The glow which is emitted while the gas returns to its normal condition is not affected by the removal of ions. It is weakened by heating, intensified by cooling. This seems to favour the view that it is due to the recombination of dissociated atoms.

(3) The modified nitrogen acts on ordinary phosphorus, combining with it, and at the same time forming much red phosphorus.

(4) It combines with sodium and also with mercury at a gentle heat, forming in the latter case an explosive compound, and in each case developing the line spectrum of the metal concerned. It also develops the line spectra of other metals, probably combining with them too.

(5) It develops the band spectra of compounds when they are vaporised in it, giving, in many cases, spectra of substances too unstable to be examined at the temperature of the Bunsen flame.

(6) It attacks nitric oxide, with formation, strangely enough, of nitrogen peroxide, a more oxidised substance.

(7) It attacks acetylene and the halogen derivatives of organic radicles, setting free the halogen, where one is present, and combining with the carbon to form cyanogen. This is proved by the brilliant cyanogen spectrum produced, and by direct chemical tests.

It may perhaps be felt that more detailed study of the compounds produced by the active nitrogen should have been made. The importance of this is not underrated, but the difficulties of working with such small quantities of material are considerable, and have led to a postponement of this branch of the work. It may be pointed out how little has been done in studying the compounds produced by ozone.

The spectroscopic data in this paper are merely general and preliminary. An accurate investigation of the various spectra by photographic methods, in collaboration with Prof. A. Fowler, F.R.S., is in progress.

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The Ionisation of Heavy Gases by X-Rays.

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Introductory Remarks.

When the term "rays" or "radiations" occurs alone in the following paper, it must be understood to mean "X-rays" or "X-radiations." The term "corpuscular rays" is limited to those corpuscles which have a velocity high enough to allow them to ionise atoms against which they strike. Corpuscles whose velocity is too small to enable them to ionise atoms will be referred to as "δ-rays."

When X-rays pass through matter, energy is absorbed from them and is known to be re-emitted in the following forms:—(1) δ-rays, (2) corpuscular rays, (3) characteristic X-rays, (4) scattered X-rays. Various relations have been found connecting the emission of these forms of energy with the substances in which they originate and with the nature of the X-rays used to produce them.

Let us consider a characteristic X-radiation produced in any substance by X-rays from any source, and let us determine the penetrating power of this radiation for a substance which does not emit a characteristic radiation—say, carbon. Then we shall define rays of higher order as those which have a greater penetrating power than this characteristic radiation, and rays of lower order as those which have a smaller penetrating power.

We may now formulate two important relations, due to Barkla and Sadler, and to Sadler, respectively:—

1. Characteristic rays can only be produced in a substance by incident rays when the latter are of higher order.*

2. The corpuscular radiation from a substance exposed to X-rays is increased when that substance is emitting its characteristic X-radiation.†

The quantitative relations, however, between these various radiations have not been fully investigated. Also the mechanism involved in the conversion of the energy of X-rays into energy of ionisation in gases is uncertain. The

* Barkla and Sadler, 'Phil. Mag.,' May, 1909.

† Sadler, 'Phil. Mag.,' March, 1910.

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latter problem has been attacked by two investigators, but with contradictory results.*

The following paper contains the results which the author has so far obtained in the investigation of these questions in the case of gases.

First Method of Investigation.

The gas used was contained in a vessel C, whose lower side was made of thin parchment paper, so that the X-rays were but slightly absorbed on entering. The region in which ionisation took place was a shallow cell D, 10 cm. in diameter and usually 1·6 cm. high. Its parallel walls were made of tightly stretched paper, and the whole vessel C was lined with aluminium covered with paper to reduce corpuscular and X-radiations from the cylindrical walls as much as possible.

A Röntgen bulb was placed at A (fig. 1), and at B various metals were

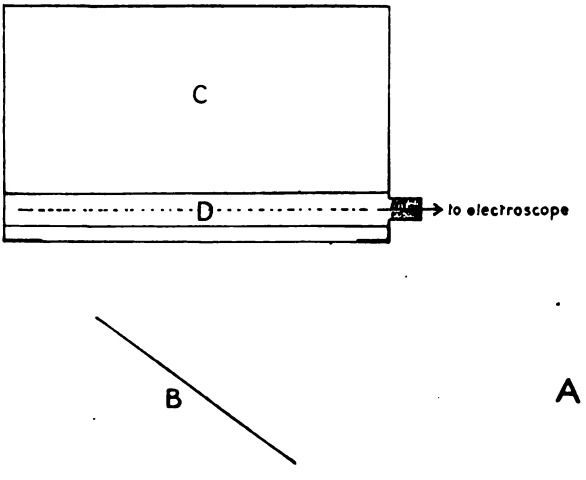

FIG. 1.

used to produce known characteristic radiations. The pressure of gas in C was varied and the change in the ionisation in D measured by an electroscope, which was an improved form of one previously described by the author.†

Let us now consider what form of curve is to be expected when ionisation is plotted against pressure, the ionisation taking place in a shallow vessel with parallel boundaries and filled with a gas which is uniformly ionised.

Let I_0 = intensity of incident X-radiation, *i.e.*, energy per cubic centimetre

* Crowther, 'Roy. Soc. Proc.,' March 10, 1909, A, vol. 82, p. 103; Bragg, 'Phil. Mag.,' September, 1910, p. 406.

† Beatty, 'Phil. Mag.,' November, 1907.

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in the incident beam. Let βI_0 = rate at which corpuscular energy is liberated per cubic centimetre of the gas at normal temperature and pressure (N.T.P.). Then $\beta I_0 p \Pi^{-1} dx$ = energy produced per second in a layer of thickness dx at pressure p, where Π = atmospheric pressure.

The portion of this energy absorbed between the layer and the upper boundary is

$$\beta I_0 p \Pi^{-1} [1 - e^{-\lambda(d-x)}] dx,$$

where d is distance between parallel boundaries and λ is coefficient of absorption of the corpuscles by the gas at pressure p.

Integrating we find that the total corpuscular energy absorbed per second between the bounding planes is

$$\beta I_0 p \Pi^{-1} [d - \lambda^{-1}(1 - e^{-\lambda d})].$$

Now let αI_0 be the energy which appears per cubic centimetre of the gas per second as ions, other than those produced during the absorption of the corpuscular energy.

Then when the pressure of the gas is p, the energy absorbed per second in this way is $\alpha I_0 p \Pi^{-1} d$. Hence total energy absorbed per second is

$$I_0 p \Pi^{-1} \{(\alpha + \beta) d - \beta \lambda^{-1}(1 - e^{-\lambda d})\}. \quad (1)$$

Now Lenard* has shown that the coefficient of absorption of corpuscular rays by matter is proportional to the density of the matter through which they pass, so that $\lambda_0 p = \lambda \Pi$, if λ_0 is the coefficient at atmospheric pressure. Also, to connect equation (1) with the amount of ionisation produced, let us assume that the same amount of energy is required to produce an ion whether the ionising agent be corpuscular rays or X-rays, and let n molecules be ionised by the expenditure of one erg, each ion so produced carrying a charge $\pm e$. Then when unit amount of energy is absorbed in producing ionisation a charge ne is given to the electrode. The ionisation produced by secondary X-radiations from the gas in the experiments to be described is very small and may be neglected.

Hence, from equation (1) we get ionisation, y, per second given by

$$y = ne I_0 p \Pi^{-1} \{(\alpha + \beta) d\} - ne\beta I_0 \lambda_0^{-1} \{1 - e^{-\lambda_0 p d \Pi^{-1}}\}, \quad (2)$$

which may be written as an expression involving p only,

$$y = Ap - B(1 - e^{-\kappa p}). \quad (3)$$

Now when the pressure of the gas is above a certain limit the exponential term in equation (3) may be neglected, and the equation reduces to

$$y = Ap - B. \quad (4)$$

* Lenard, 'Wied. Ann.,' 1895, vol. 56, p. 255.

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A comparison of the experimental curves with equation (3) will show whether corpuscular rays are produced during the ionisation of the gas. Experiments were made with $Ni(CO)_4$ and AsH_3. When radiations from silver, tin, and iodine were used curves were obtained of the form given by equation (3). The constants A, B, κ, depend of course both on the gas and the kind of radiation to which it is exposed.

Figs. 2 and 3 show two of the curves obtained. These curves thus indicate the existence of an easily absorbed radiation in the gas. Further, since the values of λ calculated from the curves agree with those previously obtained for the corpuscular rays excited in metals by the radiations from silver and tin,* we must conclude that the radiation is corpuscular.

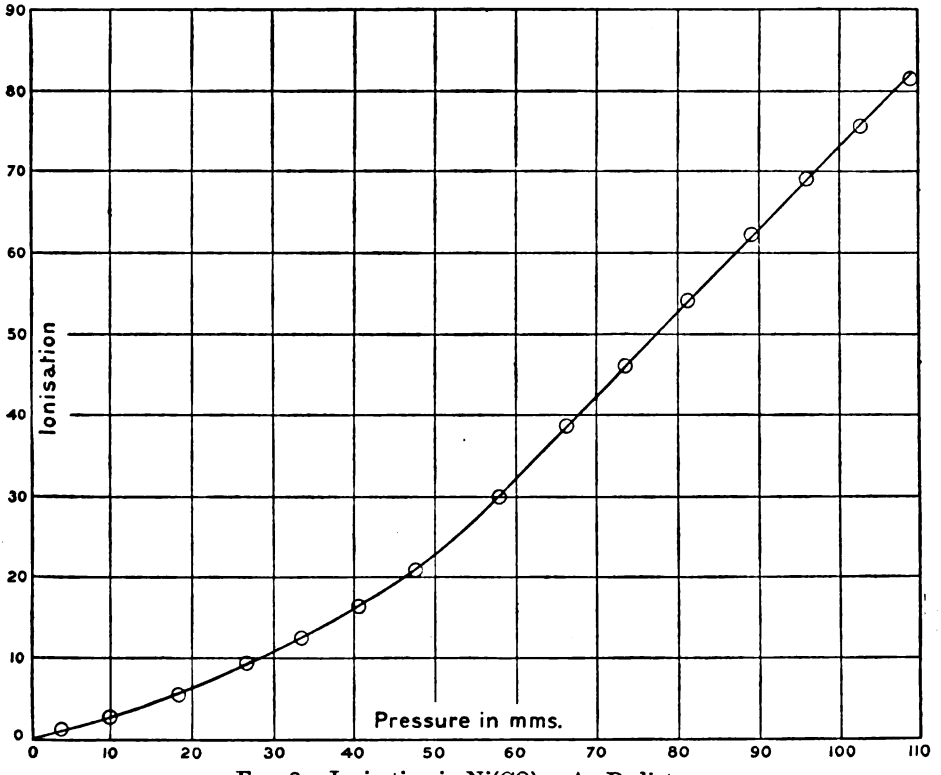

FIG. 2.—Ionisation in $Ni(CO)_4$—Ag Radiator.

In order to calculate λ and β/α from the curves let us go back to equation (4). When $y = o$ then $p = B/A$. Hence if the linear part of the curve in fig. 3 be produced to meet the axis of p

$$OA = B/A = 76\beta\{(\alpha+\beta)\lambda d\}^{-1}.$$

* Sadler, 'Phil. Mag.,' March, 1910.

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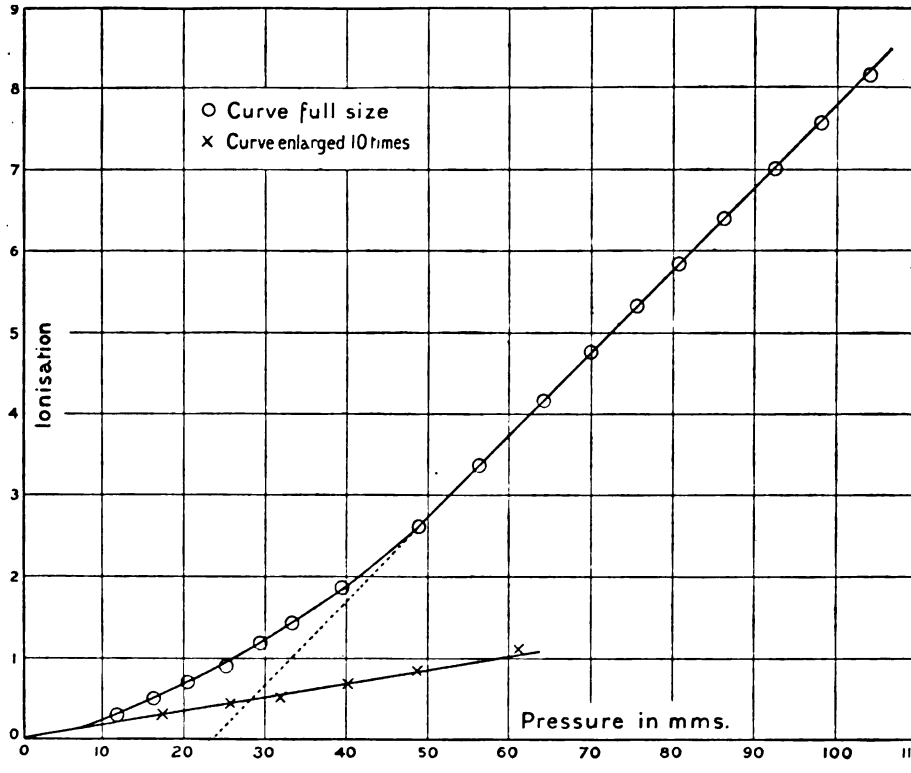

FIG. 3.—Ionisation in AsH_3—Sn Radiator.

Also from equation (2) it appears that the final slope of the curve divided by its initial slope, *i.e.*, $\tan\phi/\tan\theta$, is equal to $(\alpha+\beta)/\alpha$.

Hence we can calculate λ and β/α. These numbers were calculated in several cases and found to be in agreement with those found by the more direct method which will now be described.

Second Method of Investigation.

In equation (4) the term B results from the fact that corpuscular rays produced in the gas in the layer next to the bounding walls are stopped by those walls before their energy is entirely spent in producing ions. If the walls themselves emitted corpuscular rays at a sufficient rate to balance this loss then ionisation would become proportional to pressure. We shall now show that, if the walls of the vessel be lined with a film of the same substance as is used in the gaseous state in the chamber, this condition should be realised. For example, we might use AsH_3 in a chamber which is lined with a film of As. It is necessary that the film should be so thick that corpuscular

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rays produced at one of its surfaces should not be able to penetrate the thickness of the film so as to emerge at the other surface.

Now let βI_0 as before be the rate at which the energy of the incident rays is converted into corpuscular radiation per cubic centimetre of gas at N.T.P. Also let λ_0 be the coefficient of absorption of the corpuscular rays by the gas at N.T.P., and let D be the density of the film relative to that of the gas. Then we may assume that $\lambda_0 D$, $\beta I_0 D$, are the corresponding quantities for the film. But, assuming an exponential law of absorption, if corpuscular energy is produced per cubic centimetre of film at a rate $\beta I_0 D$, then $\beta I_0 D/\lambda D$ or BI_0/λ is the rate at which it will escape from each square centimetre of the film surface.

Of this energy $\beta I_0 \lambda^{-1}(1-e^{-\lambda d})$ will be absorbed per second by the gas in the chamber, and on adding this quantity to the right-hand side of equation (1), we finally get the following modification of equation (3) :—

$$y = Ap.^* \qquad (5)$$

In obtaining equation (5) it has been assumed that the corpuscular rays travel initially in the direction of the incident X-rays, and no account is taken of those which are deflected through more than 90° in the course of their flight. The argument would be incomplete if no account were taken of these deflected rays, but sufficient generality may be attained in the following way :—Let us assume that the corpuscular rays are initially projected in all directions. Consider those whose initial direction of motion makes with the direction of the incident X-rays an angle lying between θ and $\theta + d\theta$. Let the rate at which energy appears per cubic centimetre of gas in the form of corpuscular rays travelling in this direction be $\beta I_0 f(\theta)\, d\theta$. The author has shown† that when corpuscular rays are produced in a film of silver by X-rays which fall normally on the film, the coefficient of absorption by air of the corpuscular rays emerging from the upper surface of the film is the same as for those emerging from the lower side. We may then assume that λ is the same for each bundle of corpuscular rays, no matter what its initial direction may be.

Hence the expression $\beta I_0 \lambda_0^{-1}(1-e^{-\lambda d})$ will be replaced by

$$\int_0^{\pi} \beta f(\theta)\, d\theta\, I_0 \lambda_0^{-1}(1-e^{-\lambda d \sec\theta}).$$

But on applying the same correction to equation (1), the last term in that equation will give exactly the same integral with the sign reversed, so

* This equation has been also deduced by Prof. Bragg by a similar method. 'Phil. Mag.,' September, 1910, p. 402.

† Beatty, 'Phil. Mag.,' August, 1910.

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that the two expressions under the sign of integration cancel each other when added, and we have as before $y = Ap$.

Hence under these conditions the film radiates just enough corpuscular energy into the gas to balance the corpuscular energy lost by the gas to the walls, and ionisation becomes proportional to pressure.

In order to test equation (5), films of As and Se were deposited on the inner surfaces of the walls of the chamber when the gases AsH_3 and SeH_2 were used. Of course in these cases the film was not exactly the same substance as the gas, but the effect of the hydrogen atoms in AsH_3, for example, is quite negligible as regards ionisation effects, while the change in λ produced should entail quite a small effect and only at low pressures. Indeed, in the experimental curves it was found impossible to detect irregularities due to this cause.

When curves connecting ionisation and pressure were now drawn, it was found that in every case the curve was a straight line through the origin (fig. 4). Since a curve representing equation (5) can only be obtained if

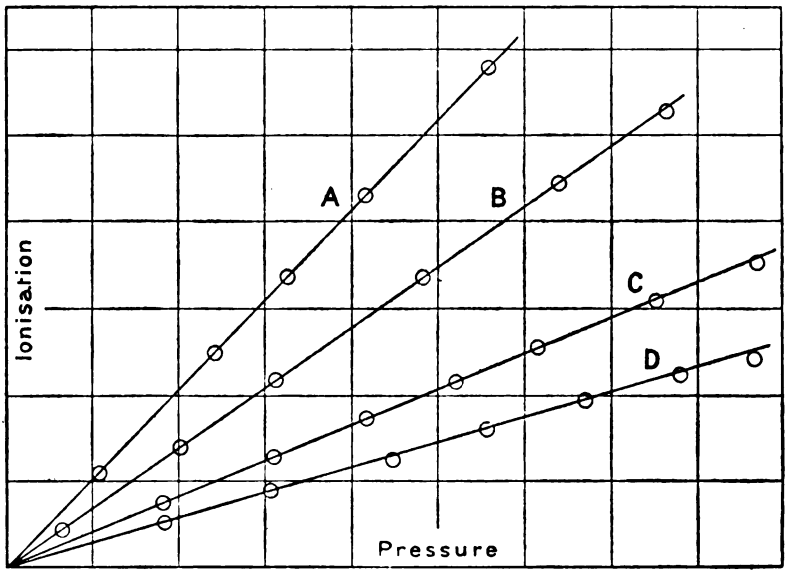

FIG. 4.—A, Ionisation in SeH_2—Sn Radiator.
B, „ AsH_3—Sn Radiator.
C, „ SeH_2—Mo Radiator.
D, „ AsH_3—Mo Radiator.

the assumption made in obtaining this equation is true, *i.e.* that the amount of corpuscular radiation produced in a substance is independent of its physical condition, we can now draw the following deductions:—

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(1) When $Ni(CO)_4$, AsH_3, SeH_2, are ionised by radiations of higher order, corpuscular radiation is produced in the gas or vapour.

(2) This corpuscular radiation is produced in the same quantity per gramme of the substance, whether the substance is in the solid or gaseous condition.

With regard to these deductions there is no reason to suppose that Ni, As, Se, are exceptional in their behaviour towards radiations, and there is much evidence to show that the above conclusions may be extended to many other chemical elements.

The next step was to find how much of the ionisation in the gas was due to the ions formed during the absorption of the corpuscular radiation produced in the gas. Consider a vessel, 1 cm. in height, containing air, and bounded by two parallel films of Se. Let i be the ionisation produced per second by the incident X-rays in the air in the vessel. Let Ri be the ionisation per second in the air due to corpuscular radiation from the films. Then

$$Ri = ane\beta I_0 \lambda_0^{-1}, \tag{6}$$

where a is the combined area of the films, and λ_0 is the coefficient of absorption of the corpuscular rays by SeH_2 at N.T.P.

Now, if ρ is the density of SeH_2 relative to that of air at the same pressure, and μ the coefficient of absorption of the corpuscular rays by air, then, assuming Lenard's law,

$$\lambda_0 = \rho\mu. \tag{7}$$

On eliminating λ_0 from (6) and (7) we get

$$R\mu\rho = ane\beta I_0/i. \tag{8}$$

Now βI_0 is the rate at which corpuscular energy is produced in SeH_2 per cubic centimetre, so that the right-hand side of equation (8) represents the ionisation per cubic centimetre in SeH_2 due to corpuscular radiation, relative to that in air at the same pressure due to the incident X-rays.

The following experiments were made to find R and μ. The chamber C (fig. 1) was filled with air, and the inside of the ionisation vessel was lined with a film of Se. The air-pressure was varied, and ionisation plotted against pressure. Fig. 5 is a type of the curve obtained.

In Fig. 5, c evidently represents the ionisation due to corpuscular energy from the films.

b represents the ionisation in air at 760 mm. pressure, due to the incident X-rays. Since the ionisation vessel was 1·6 cm. in height, $b/1{\cdot}6$ represents the ionisation in a space 1 cm. thick. Hence $1{\cdot}6\ c/b = R$. Also μ, the

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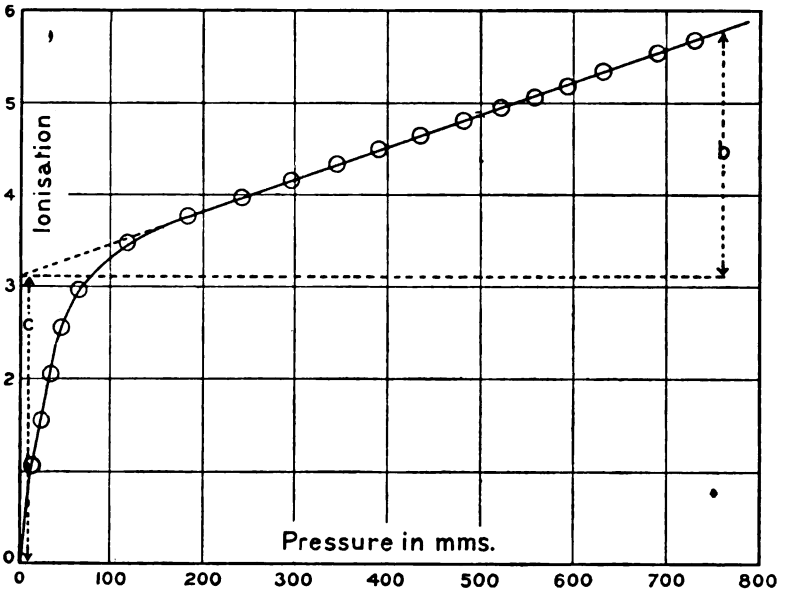

Fig. 5.—Se Radiator.

coefficient of the corpuscular rays from the films, can be determined from the curve in fig. 5 in the manner described in a previous paper.*

The values of $R\mu\rho$ are given in Table I, Column 4. To obtain the total ionisation in SeH_2 relative to that in air, the ionisation in the vessel was measured at different pressures when the vessel was occupied by (1) pure SeH_2, (2) air. The ratio of the slopes of the linear parts of the curves thus obtained gives the total ionisation in SeH_2 relative to that in air for any particular radiator.

The values of the relative total ionisation are given in Table I, Column 5.

Table I.—Ionisation in SeH_2 relative to that in Air.

Radiator.	R.	λ.	Ionisation due to corpuscular rays = $R\lambda\rho$.	Total ionisation.	Total ionisation minus corpuscular ionisation.
Fe	Values not yet completely determined			30·3	
Cu				29·2	
Se.....				30·6	
Sr.....	1·98	16·1	92	122	30
Mo	2·56	14·0	103	190	87
Ag	4·78	8·8	121	231	110
Sn	7·2	6·5	135	250	115
I	10·8	5·9	183	286	103

* Beatty, 'Camb. Phil. Soc. Proc.,' vol. 15, Pt. 5, p. 416.

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Examination of Table I.

From Column 5 we see that the ionisation in SeH_2 relative to that in air remains constant till the characteristic X-radiation of Se is evoked. When radiations of higher order are used the ionisation is greatly increased.

Let us now consider the corpuscular energy coming from the films. When radiations of lower order are used an easily absorbed radiation is emitted from the films, but it is not yet certain that it is entirely corpuscular, and at present no quantitative results are given for it in the table. When we pass to radiations of higher order a large increase of corpuscular energy is found, accounting for the greater part of the whole ionisation produced.

To what is the remainder of the ionisation due, *i.e.*, the ionisation given in Column 6? It cannot be accounted for by the absorption of the characteristic X-radiation produced in SeH_2, for at the pressures used the fraction of this radiation absorbed is negligible.

Three possibilities, at least, present themselves. The remainder may be due to the direct formation of ions by the incident X-rays, to a discharge of δ-rays from the atom at the moment when the corpuscle leaves it, or to a similar discharge due to the disturbances produced in the atom by the excitation of the characteristic radiation.

Experiments are now in progress to determine the amount of energy emitted by the gas in the form of characteristic radiation. The results so obtained will assist in deciding between the possibilities mentioned. The emission of corpuscular rays when radiations of lower order are used is also being closely examined. From results already obtained it seems that these rays may account for an appreciable fraction of the whole ionisation, even when the characteristic radiation is not evoked.

Summary.

1. When X-rays pass through AsH_3, SeH_2, or $Ni(CO)_4$, a large part of the ionisation produced is due to the production of corpuscular rays.

2. The corpuscular rays are produced in the same quantity from these substances whether they are in the solid or the gaseous condition.

3. The case of SeH_2 has been closely examined and quantitative results found for the fraction of the total ionisation due to corpuscular rays.

I desire to thank Prof. Sir J. J. Thomson for his interest in and helpful criticism of the above work.

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The Variation of Ionisation with Velocity for the β-Particles.

By W. Wilson, M.Sc., Honorary Fellow of the University of Manchester.

(Communicated by Prof. E. Rutherford, F.R.S. Received February 18,—Read March 23, 1911.)

Although many researches have been made on the properties of the β-rays, no results have so far been published giving the variation of the ionisation due to them with their velocity. Durack* has shown that the β-rays from radium are less efficient ionisers than the cathode rays from a discharge tube, but no law of variation can be formulated from his experiments. A determination of this variation is of importance, since most experiments with the β-rays, *e.g.* those dealing with their absorption by matter, have been made by measuring the ionisation in a vessel through which the β-particles were passing, and such experiments do not give definite information about the actual number of particles involved unless the variation of the ionisation of the β-particles with velocity is known.

The following experiments have been made with a view of finding this relation, and the results show that the ionisation per centimetre of path is inversely proportional to the square of the velocity of the particles.

The method adopted was to separate out rays of different velocities by means of a magnetic field from the heterogeneous beam given out by Radium B and C. The charges carried by the particles of each velocity and the corresponding ionisations were measured, and the relative ionisation per particle at different velocities thus determined.

Apparatus.

The arrangement of apparatus used in the measurement of the first of these quantities is shown in fig. 1.

The source of radiation was a quantity of radium emanation (corresponding to about 150 milligrammes radium bromide) contained in a thin-walled bulb A which was fixed in position by means of a ground glass joint B. The rays passed into a flat brass box C, fixed between the pole pieces of an electromagnet, were bent round by the magnetic field, and entered the copper vessel E. The screens and walls of the vessel C were covered with cardboard in order to reduce the effects due to the secondary and scattered rays. The walls of E were so thick (2·5 mm.) as to be able to absorb any β-particles which fell on them. The length of E was 4 cm. and its diameter 3·3 cm.

* 'Phil. Mag.,' VI, 4, 1902, p. 29 ; and VI, 5, 1903, p. 550.

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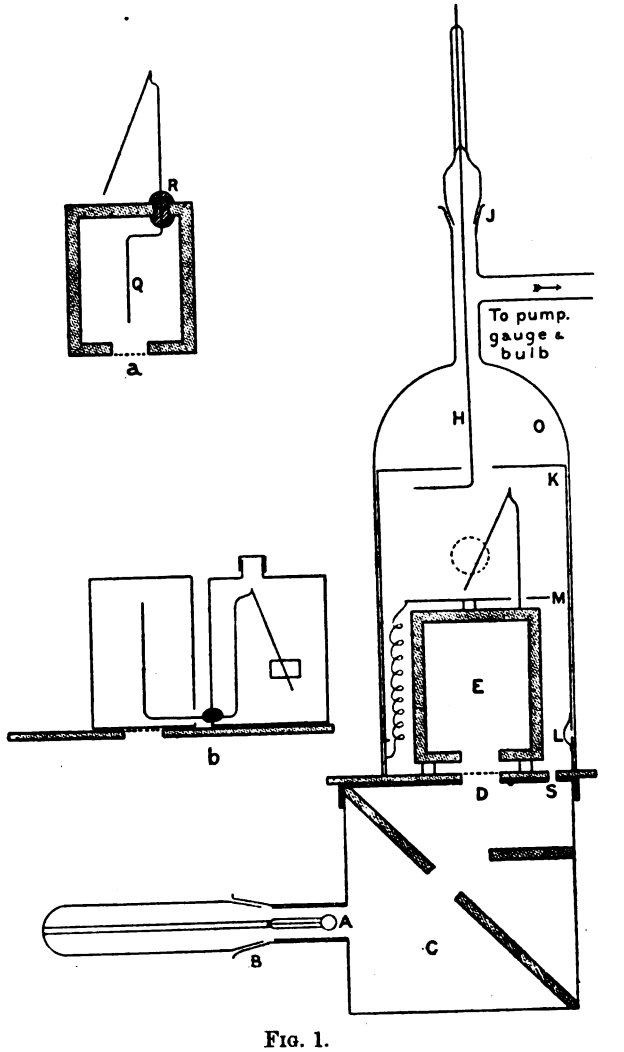

FIG. 1.

It was supported on three ebonite studs, and thus insulated. This method of catching the β-rays was adopted in order that the error due to the reflexion of the particles should be as small as possible, since only a small proportion of the reflected rays would be able to escape through the opening in the cylinder.

A standard to which a gold leaf was attached was carried by E, and the system could be charged by means of a rod H. This rod could be turned about a vertical axis, leakage of air into the apparatus being prevented by the ground glass joint J.

The gold-leaf system was surrounded by a brass tube K which screened it

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from electrostatic effects. This screen was joined to earth through a spring L. When the gold leaf was charged it was found to be unstable owing to the repulsion of the charge on E, and was therefore screened by means of an earthed plate M insulated from E by an ebonite plug.

The whole was enclosed in a glass vessel O, which was fastened with sealing wax to the lid of C, and could be exhausted along with the vessel C by a Fleuss pump. The final stage of exhaustion was carried out by means of a charcoal bulb immersed in liquid air. The pressure in the vessel was determined by means of a McLeod gauge, and was of the order 1/1000 mm. of mercury.

In performing an experiment the cylinder was first charged positively, and the rate of fall of the leaf determined. It was then charged to the corresponding negative potential and the rate of rise determined. The leaf was charged by means of a battery of 200 Clarke cells.

Now besides the negative charge gained by E due to the absorption of the β-particles, there is a leak of electricity from E to earth due to the ionisation in the residual air by the β-rays and the γ-rays from the source of radiation. In the first case the fall of potential of the leaf is due to the sum of the effects due to absorption and ionisation. In the second case the ionisation acts against the effect due to absorption, so that the mean of the two readings gives us the effect due to the absorption of the β-particles alone. Thus in an actual experiment the leaf fell with a velocity of 1·17 divisions per minute, when the vessel was charged positively, and rose with a velocity of 0·88 division per minute when it was charged negatively. The effect due to the β-particles alone, therefore, was 1·02 divisions per minute. This was repeated with the rays passing through magnetic fields of various strengths, so that the charge carried by the β-particles corresponding to the various velocities was determined. This charge is proportional to the number of particles entering the vessel, since each particle has the same electrical charge. The actual number of particles was not determined owing to the difficulty of measuring the capacity of the gold-leaf system.

The radius of curvature of the path of the rays was 3·5 cm. and the magnetic field was determined by means of a Grassot fluxmeter which was calibrated. The velocity was deduced from the product of the magnetic field and radius of curvature of the rays by means of the equations

$$\mathrm{H}\rho = \frac{mv}{e}, \qquad \frac{e}{m} = \frac{e}{m_0}\left(1-\frac{v^2}{c^2}\right)^{\frac{1}{2}},$$

the latter being that required by the phenomena of relativity; where H is the value of the magnetic field, ρ the radius of curvature, v the velocity of the

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rays, and c the velocity of light. The value of e/m_0 was taken as $1{\cdot}74 \times 10^7$ E.M.U.*

To determine the ionisation due to the particles of different velocities the apparatus was modified as follows:—The cylinder E was removed and replaced by another of exactly the same size and shape, but which was connected to earth instead of being insulated (fig. 1*a*). A central rod Q was insulated from the vessel by a sulphur plug R, and carried a gold leaf by means of which the ionisation inside the vessel could be measured. The ionisation was determined at low pressures, viz., from 0·1 to 5 cm. of mercury, and was found to be proportional to the pressure. The opening was closed by a gold leaf in order to prevent the entrance of stray ions from the outside.

Now in these experiments the ionisation is increased by the reflexion of β-particles from the sides of the vessel. The amount of increase is different for different velocities, and a special experiment was made to determine the correction to be applied.

A cage of thin wire of the same size as the internal dimensions of the ionisation vessel was made as shown in fig. 1*b* and was covered with thin aluminium leaf. It stood on a plate of copper in which was a hole of the same size as that of E. This ionisation vessel was connected to an electroscope and the ionisation in it could be determined. A copper vessel of the same size as E but without bottom was made, and could be placed over the cage or removed at will. The proportional increase of ionisation when the copper vessel was on was found to be substantially the same as that determined for multiple reflexion between two plates by Kovarik and Wilson.† The results obtained could thus be corrected for the reflexion of particles from the sides of the vessel.

Results.

Experiments were made under two conditions. In the first experiments the hole D was closed by a thin sheet of mica covered with gold leaf. This was done in order to prevent spurious effects due to the ions formed in the vessel C being dragged into E by the electric field. A small hole S ensured the free passage of the air from C to O during exhaustion.

Results obtained are shown in Table I. It will be seen that the ionisation varies approximately inversely as the velocity for the lower velocities and as the square of the velocity for the higher.

* Bucherer, 'Phys. Zeit.,' 1908, vol. 9, p. 755.

† Kovarik and Wilson, 'Phil. Mag.,' November, 1910.

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Table I.

$H\rho$. (Gauss cm.).	Velocity, v. 10^{10} cm./sec.	No. of β-particles (charge). Arbitrary units.	Ionisation.	Ionisation corrected for reflexion.	$\frac{\text{Ionisation}}{\text{Charge}} = I$.	Iv.	Iv^2.	Iv^3.
770	1·24	66·0	22·5	22·5	341×10^{-3}	42	53	65
1060	1·56	90·0	29·5	25·0	278×10^{-3}	43	68	106
1350	1·85	104·0	32·5	23·9	230×10^{-3}	42	79	146
1650	2·20	112·0	33·5	22·0	196×10^{-3}	43	95	209
1940	2·25	116·0	33·0	20·5	163×10^{-3}	37	82	186
2180	2·36	119·5	31·2	18·8	157×10^{-3}	37	87	206
2440	2·49	119·5	29·0	17·0	142×10^{-3}	35	88	219
2710	2·54	116·0	26·5	15·2	131×10^{-3}	33	85	215
2980	2·60	109·0	24·2	13·7	126×10^{-3}	33	85	221
3240	2·66	101·0	22·0	12·4	123×10^{-3}	33	87	232
3500	2·70	94·0	20·0	11·3	120×10^{-3}	32	87	235
3720	2·72	88·5	18·3	10·3	116×10^{-3}	32	86	234
3960	2·75	82·0	16·5	9·3	113×10^{-3}	31	86	235
4630	2·81	68·5	12·7	7·2	105×10^{-3}	29	83	234
5420	2·86	53·5	9·6	5·6	105×10^{-3}	30	86	245
6300	2·90	41·0	7·8	4·8	117×10^{-3}	34	98	285

Now owing to the small charge carried by the rays it is impossible to work with very narrow pencils, and thus the rays sorted out are only approximately homogeneous. The error due to this would be especially marked for the very slow rays, since they are few in number, and the scattered β-particles of higher velocity which get into the vessel are thus relatively important. Further, we have seen that the hole D was closed by a mica window, and since the slow rays are very easily absorbed the proportion of swift to slow rays would be increased.

Thus, since the slow rays ionise more per centimetre of path than the swift rays, it follows that the ionisation for the rays corresponding to low magnetic fields will be less in proportion to the number of particles than it would be if the rays were more homogeneous and scattered rays were prevented from entering.

The apparatus was therefore modified as follows:—The mica was replaced by a thin gold leaf and the screens were altered so as to produce a better definition of the beam. This is the arrangement shown in fig. 1, and the results obtained are shown in Table II and graphically in fig. 2. The circles denote the experimental values, and the curves a, b, c are drawn on the assumption that the ionisation varies inversely as the first, second, and third power of the velocity respectively. It is at once apparent that the results agree much more closely with the second power law than with either of the others.

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Table II.

$H\rho$. Gauss cm.	v. 10^{10} cm./sec.	No. of particles (charge).	Ionisation.	Ionisation corrected for reflexion.	$\frac{\text{Ionisation}}{\text{Charge}} = I$.	Iv.	Iv^2.	Iv^3.
850	1·35	49	7·67	7·67	15·7	21·2	28	38
1150	1·66	73	9·82	8·31	11·4	20·6	31	52
1390	1·87	87	10·99	8·10	9·3	17·8	32	61
1650	2·08	105	10·97	7·20	6·85	14·3	30	62
1890	2·23	106	10·47	6·50	6·14	13·7	30	71
2160	2·35	108	9·77	5·89	5·45	12·8	30	71
2440	2·46	102	8·64	5·06	4·95	12·2	30	74
2750	2·55	104	7·82	4·66	4·48	11·4	29	74
3300	2·67	89	6·44	3·63	4·08	10·9	29	78
3900	2·74	76	5·43	3·06	4·03	11·0	30	83
4800	2·82	56	3·82	2·16	3·86	10·9	31	87
5430	2·86	47	2·97	1·71	3·64	10·4	30	85
5910	2·88	44	2·58	1·52	3·46	9·9	29	83
6350	2·90	39	2·23	1·37	3·52	10·2	30	86

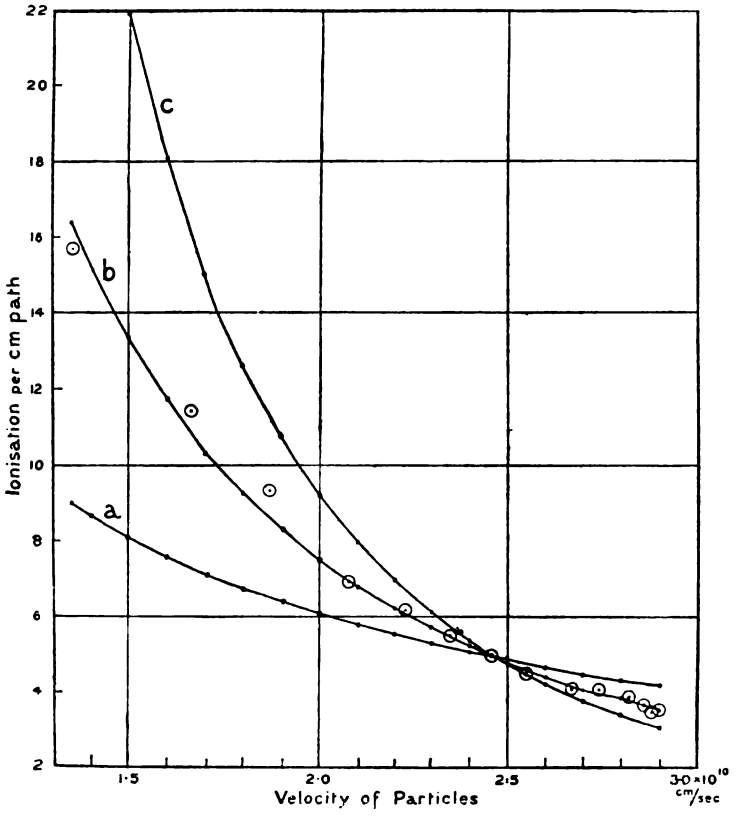

FIG. 2.—*a* is the curve $I = k_1/v$; *b* is the curve $I = k_2/v^2$; *c* is the curve $I = k_3/v^3$.

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These results can be easily accounted for in the following manner.

Consider a large number of β-particles of velocity v passing through matter. The average time t spent by a particle in the neighbourhood of an atom is as $1/v$. Let the average force exerted on an electron in the atom by a β-particle be F. The distance moved by the electron in time t will be $\frac{1}{2}ft^2$, where f is the acceleration, and the work done will be $\frac{1}{2}Fft^2$.

Now, if the same amount of energy is required for the production of each ion, the ionisation should be proportional to the work done by the β-particle, or to At^2, where A is some constant. Since t varies as $1/v$, the ionisation should vary inversely as the square of the velocity.

Ionisation in a Thick Copper Vessel.

Nearly all measurements of ionisation have been made with vessels thick enough to reflect a large proportion of the rays which fall on the walls, and the connection between the ionisation in the thick copper vessels used above and velocity is shown in Tables III and IV, which correspond respectively to the two sets of results given in Tables I and II. The values given in Table IV are shown graphically in fig. 3.

Table III.

$H\rho$. Gauss cm.	v. 10^{10} cm./sec.	$\frac{\text{Ionisation}}{\text{Charge}} = I$.	Iv.	Iv^2.
770	1·24	34·1	42	53
1060	1·56	32·8	51	80
1350	1·85	31·2	58	108
1650	2·20	29·9	66	144
1940	2·25	28·3	64	144
2180	2·36	26·1	62	146
2440	2·49	24·3	61	151
2710	2·54	23·2	59	150
2980	2·60	22·2	58	150
3240	2·66	21·8	58	152
3500	2·70	21·3	58	156
3720	2·72	21·6	59	160
3960	2·75	20·1	50	152
4630	2·81	18·6	52	147
5420	2·86	17·9	51	146
6300	2·90	19·0	55	160

We see that in this case the ionisation is not connected with the velocity by any simple power law. This is to be expected, on account of the complicated manner in which β-particles are scattered.*

* See Kovarik and Wilson, *loc. cit.*

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Table IV.

$H\rho$. Gauss cm.	v. 10^{10} cm./sec.	$\frac{\text{Ionisation}}{\text{Charge}} = I$.	Iv.	Iv^2.
850	1·35	156	21	28
1150	1·66	134	22	40
1390	1·87	126	24	44
1650	2·08	104	22	45
1890	2·23	99	22	49
2160	2·35	90	21	50
2440	2·46	85	21	52
2750	2·55	75	19	49
3300	2·67	72	19	51
3900	2·74	71	19	53
4800	2·82	68	19	54
5430	2·86	63	18	51
5910	2·88	59	17	49
6350	2·90	57	16	48

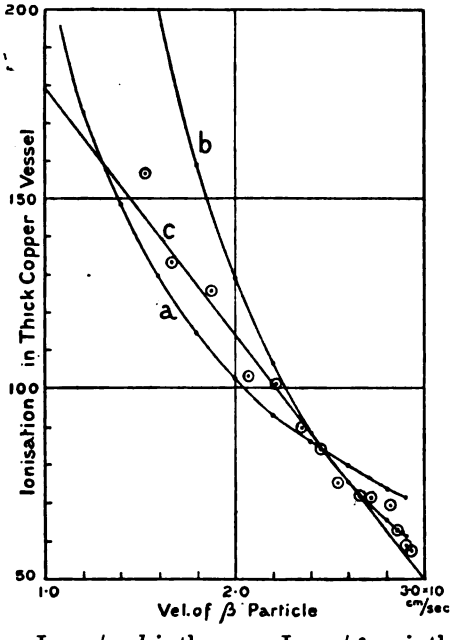

FIG. 3.—a is the curve $I = c_1/v$; b is the curve $I = c_2/v^2$; c is the curve $I = k'(c-v)$.

The ionisation under these circumstances, as will be seen from fig. 3, can, between the limits examined, be approximately represented by

$$I = k(c-v),$$

where I is the ionisation, v the velocity, c and k are constants.

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Conclusions.

1. The ionisation produced per centimetre by β-particles in free air varies inversely as the square of the velocity between the limits examined.

2. The ionisation in a thick copper vessel is not connected with the velocity by any simple power law, but is approximately given by $I = k(c-v)$, where k and c are constants and v the velocity of the β-particles.

In conclusion, I wish to express my best thanks to Prof. Rutherford for proposing this research, and for his suggestions from time to time during its progress.

The Association of Lead with Uranium in Rock-Minerals, and its Application to the Measurement of Geological Time.

By Arthur Holmes, A.R.C.S., B.Sc., Imperial College of Science and Technology.

(Communicated by Prof. the Hon. R. J. Strutt, F.R.S. Received March 20,—Read April 6, 1911.)

1. *Introduction.*—The study of radioactive minerals is of great importance from two points of view. Such minerals may be regarded as storehouses for the various series of genetically connected radioactive elements. In them the parent element slowly disintegrates, while the ultimate products of the transformation gradually accumulate. The analysis of these minerals ought, then, in the first place, to disclose the nature of the ultimate product of each series; secondly, a knowledge of the rate of formation of this product, and of the total quantity accumulated, gives the requisite data for a calculation of the age of the mineral.

It has been shown that the disintegration of uranium results in the formation of eight atoms of helium.* In 1907 Boltwood brought forward strong evidence suggesting that lead is the ultimate product of this disintegration.† In this paper it is hoped to produce additional evidence that such is the case, according to the following equation:—

$$\begin{array}{ccccc} U & \rightarrow & 8He & + & Pb. \\ 238{\cdot}5 & & 32 & & 2{\cdot}069. \end{array}$$

* See Strutt, 'Roy. Soc. Proc.,' A, 1908, vol. 81, p. 276.

† Boltwood, 'Am. Journ. Sci.,' 1907, p. 77.

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On the assumption that helium is produced to this extent, Rutherford has given data* from which it may be calculated that 1 gramme of uranium produces $10{\cdot}7 \times 10^{-8}$ c.c. of helium per annum. Strutt has verified this theoretical estimate by a direct appeal to experiment.† Actually measuring the annual production of helium, he obtained a corresponding result of $9{\cdot}9 \times 10^{-8}$ c.c. Accepting the theoretical figure, which is equivalent to $1{\cdot}88 \times 10^{-11}$ grm., it is easily calculated that the amount of lead which would remain is $1{\cdot}22 \times 10^{-10}$ grm. per gramme of uranium per annum. If this rate of production were constant, a gramme-molecule of lead would take the place of a gramme-molecule of uranium in 8,200 million years. However, the rate is not constant, but is proportional to the amount of uranium remaining unchanged. If the latter is large compared with the total amount of lead produced, the rate may be taken as nearly constant, and the age of the mineral in which this disintegration has occurred is given by

$$\mathrm{Pb/U} \,.\, 8200 \times 10^6 \text{ years},$$

where Pb and U represent the respective percentages of these elements at the present day. In many cases, however, this constancy cannot be assumed, and it is necessary to substitute for the present-day percentage of uranium its time-average for the period considered. Thus, in the minerals described in this paper, the difference between the uranium now present and that originally present amounts to about 5 per cent., and, in calculating the age, corresponding values are obtained. In this case a sufficiently accurate approximation to the time-average is given by the mean.

For minerals of the same age, the ratio Pb/U should be constant, if all the lead has originated as suggested. Further, for minerals of different ages, the value of Pb/U should be greater or less in direct proportion to those ages.

Collecting all the known analyses of primary uranium-bearing minerals which included a determination of lead, Boltwood‡ showed that the above conditions were generally found to hold. Unfortunately, he omitted to give the geological ages of the several occurrences. In a summary of his analyses, to be given in a later section, these will be indicated as accurately as at present is possible.

2. *Selection of Minerals.*—In order that the suggested relations between lead and uranium should be detectable, and that lead should be confidently used as a reliable age-index, certain assumptions require to be made. The selection of minerals must be such that for them these assumptions are justifiable. They will be considered as follows:—

* Cited by Strutt, 'Roy. Soc. Proc.,' 1908, p. 276.

† Strutt, 'Roy. Soc. Proc.,' A, 1910, vol. 84, p. 388.

‡ 'Am. Journ. Sci.,' 1907, p. 77.

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(*a*) That no appreciable amount of lead was present when the mineral was formed.

(*b*) That no lead has originated by any other radioactive process than that suggested.

(*c*) That no lead nor uranium has subsequently been added or removed by external agencies.

(*a*) Previously to the consolidation of a rock magma, the uranium in the latter must, of course, have been generating helium and lead for an unknown period. It is probable that much of the lead then present would, at the time of crystallization, be carried away in hot sulphide solutions to form the hydatogenetic and metasomatic deposits of lead which provide our supplies of that metal. Doubtless, however, a certain amount of lead would be retained in the molecular network of crystals, and consequently analyses of a rock as a whole should give values of Pb/U higher than that corresponding to the period since consolidation. This difficulty may be avoided by considering particular minerals. Thorite, zircon, in some cases apatite and sphene, and other rarer minerals segregate within themselves on crystallization a much larger percentage of uranium than remains to the rest of the magma. Within these minerals lead accumulates to such an extent that the amount originally present becomes negligible.

(*b*) It may be objected that lead may perhaps originate as a product of some element other than uranium. Boltwood shows that it is highly improbable that thorium should give rise to lead, and the results submitted in this paper add further proof to that independence. Wherever lead occurs in primary minerals it is associated with uranium, and there is little doubt that it can be completely accounted for in this way.

(*c*) It may seem unlikely that for periods of hundreds of millions of years a mineral should remain unchanged by external chemical agencies. In the earth's surface materials, making up the belt of weathering, solution is the dominant process. Lower down, in the belt of cementation, re-deposition is more characteristic.* Can we be sure that these processes have not dissolved out lead or uranium at one time, depositing the same elements at another time? In some cases we cannot, but, fortunately for our purpose, many of the uranium-bearing minerals, like zircon, are dense and stable, and capable of withstanding great changes in their environment without undergoing alteration. But an appeal to analysis will rarely fail to dispel this difficulty. If such changes have occurred, it is inconceivable that they would always have affected lead and uranium in the same proportion,

* See Van Hise, "Treatise on Metamorphism," 'Mon. United States Geol. Survey,' 1904, vol. 47.

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and hence the results obtained from different minerals should show marked discrepancies. On the other hand, if the analyses give consistent results one can only assume that any alteration has been inappreciable. A microscopical examination of the minerals in question affords a useful guide to the extent of alteration. Unless one can be sure in this way that the mineral is fresh, it is clear that reliable results can only be expected when a series of minerals are examined.

Still another possible objection may be treated here. Under the high temperatures and pressures which rocks have undergone during their geological history, is it safe to assume that radioactive changes proceed at the same rate? All that can be said is that experimental evidence consistently agrees in suggesting that these processes are quite independent of the temperatures and pressures which igneous rocks can have sustained without becoming metamorphosed. Arrhenius has supposed that radioactive processes may be reversed under the conditions prevailing at great depths. This idea has nothing but analogy to support it. There is abundant evidence that molecular changes are reversed at greater depths, *e.g.*, in the upper zones of the earth's crust silicates are replaced by carbonates, while in the lower zones carbonates are decomposed and silicates are formed. But that interatomic changes should reverse, or even proceed more slowly or quickly, there is no evidence.

From these considerations, it is obvious that the only minerals to be chosen are fresh, stable, primary rock-minerals. Secondary and metamorphic minerals could not be relied upon to satisfy the required conditions. There occurs in the Christiania district of Norway,* a geologically depressed area of nearly 4,000 square miles, which is separated on every side by faults from the surrounding Pre-Cambrian gneiss. In this area there is a nearly complete sequence of early palæozoic rocks. Above these strata there are a few beds of red sandstone of Lower Devonian age. Over these beds and intercalated with them are lava flows; and, finally, penetrating the whole mass, representing a later phase of this period of igneous activity, are great intrusions of plutonic rocks. Amongst the earliest of the intrusions is a series of thorite-bearing nepheline-syenites. Brögger believes them to be of Middle or Lower Devonian age, most probably the latter. The minerals occurring in them are, in many instances, notably radioactive, and thus they afford an admirable series in which to investigate the consanguinity of lead and uranium. Several of these minerals were obtained from Brevig, and estimations of these elements in each case were made.

* See Brögger, 'Zeit. für Kryst,' 1890, vol. 16.

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3. *Methods of Analysis.*—(a) *Uranium.*—This constituent was estimated by Strutt's method,* in which radium emanation is directly measured, and the constancy of its ratio to uranium used to give the amount of the latter.

From 0·3 grm. to 2·0 grm. of the finely powdered mineral was used for each estimation, according to the relative richness of the mineral in uranium. From preliminary electroscopic tests this could be roughly measured. The powdered mineral was fused with borax in a platinum crucible, and the resultant glass dissolved in dilute hydrochloric acid. After boiling, and standing for several days in a corked flask, the radium emanation was boiled out, collected in a gas-holder, and ultimately transferred to an electroscope. Knowing the normal leak and constant of the electroscope, a measurement of leak sufficed to give the necessary data for the calculation of the equivalent amount of uranium.

Blank experiments were made with the reagents used, and the normal leak was determined at suitable times throughout the investigations. In no case was any appreciable difference observed. Two solutions of each mineral were made, and two estimations of each. Without exception, the results obtained agreed closely.

(b) *Lead.*—Several methods of estimating lead were attempted, but the most constant and reliable results were found to be attained by weighing it as sulphate, and in cases when the quantity of lead present was too small for the gravimetric method, colorimetric estimations were made.

Gravimetric method.—Quantities varying up to nearly 100 grm. of the finely powdered mineral were intimately mixed with four or five times as much fusion mixture, and fused in a platinum basin. On allowing the melt to cool completely, the cake could usually be easily separated by treating with boiling water. A second heating and cooling always resulted in a successful separation. The cake was broken up by boiling with water in a beaker. Dilute hydrochloric acid was gently heated in the platinum basin to remove any still adherent portions of the cake. The contents of the basin were then washed into the beaker, and more hydrochloric acid added. The solution thus formed (with a colloidal mass of silica) was evaporated to dryness, and, dilute hydrochloric acid having been added, this was repeated a second time. On again adding dilute acid and heating, the silica was easily filtered off, leaving a clear solution. From the latter lead was precipitated as sulphide, by heating and adding ammonium sulphide. The precipitate was collected on as small a filter paper as possible, dried and ignited. The residue was treated with a little nitric acid, and boiled to convert any reduced lead to nitrate. Sulphuric acid was finally added, and the whole heated until all nitric

* 'Roy. Soc. Proc.,' A, 1906, p. 473 *et seq.*

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acid fumes had ceased. A tiny white precipitate then remained. This was collected on a very small filter, of which the weight of the ash was accurately known, washed with alcohol, dried, ignited, and weighed with the greatest possible accuracy.

*Colorimetric method.**—Standard solutions containing known quantities of lead, as nitrate, were prepared by dissolving the lead compound in a slightly acidified solution containing ammonium acetate and grape sugar, known as the " diluting solution.

The lead to be estimated having been concentrated in a nitric acid solution as already described, the latter was evaporated to dryness, or nearly so. The residue was then taken up with a little of the diluting solution. This was treated with a known quantity of well-diluted ammonium sulphide, the liquids being contained in a graduated glass vessel. A brown coloration was produced. One of the standard solutions was similarly treated in an exactly similar vessel. The diluting solution was then added to one vessel or the other until the colours produced in both were indistinguishable, care being taken that the amount of ammonium sulphide in each was proportionate to the respective volume. After a little practice with solutions of known strengths, this could be done with confidence, and concordant results were obtained. Tested by the sulphate methods slightly higher results were given in general.

The colorimetric method obviously assumes the absence of copper and bismuth.

From Vogt's estimates of the average amount of these metals in 100 grm. of rock :—†

	Grm.
Lead	$0{\cdot}000x$
Copper	$0{\cdot}0000x$
Bismuth	$0{\cdot}00000x$

it might be anticipated that the latter two would not have much influence. Tests were, however, applied to detect any very small quantities which might be present. By testing for copper‡ with hydrobromic acid, about 0·00002 grm. was probably the greatest amount indicated. Schneider's test applied for bismuth§ failed to detect that element. To the fourth decimal the amount of lead was therefore unaffected by its non-separation from copper or bismuth.

The smallest amount of lead estimated, viz., 0·0003 grm. in 100 grm. of

* V. Harcourt, 'Journ. Chem. Soc.,' 1910, vol. 97, p. 841.
† 'Zeit. prakt. Geol.,' 1898.
‡ 'Select Methods of Chemical Analysis,' Crookes, 1905, p. 295.
§ *Ibid.*, 1905, p. 355.

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felspar, approaches the limit to which the colorimetric method can be applied quantitatively, although smaller quantities than this can easily be detected.

4. *Experimental Results.*—The results obtained are tabulated below:—

Mineral.	Uranium. Grm. per 100 grm. mineral.	Lead. Grm. per 100 grm. mineral.	Pb/U.
Thorite (1)	10·1040	0·4279	0·042
Orangite (1)	1·2437	0·0570	0·046
Orangite (2)	1·1825	0·0542	0·046
Thorite (2)	0·4072	0·0196	0·048
Homelite	0·2442	0·0121	0·049
Zircon	0·1941	0·0085	0·044
Pyrochlore (1)	0·1923	0·0120	0·062
Pyrochlore (2)	0·1855	0·0093	0·050
Biotite	0·1602	0·0069	0·043
Tritomite	0·0631	0·0026	0·041
Freyalite	0·0526	0·0028	0·053
Mosandrite	0·0432	0·0024	0·056
Eagerine	0·0253	0·0015	0·060
Astrophyllite	0·0140	0·0007	0·050
Catapleite	0·0132	0·0009	0·068
Nepheline	0·0010	0·0004	0·400
Felspar	0·0006	0·0003	0·500

With the exception of pyrochlore, specimen (1), and astrophyllite, the number of lead estimations varied from two to five. Of the minerals named, only one determination was made, owing to lack of material. It will be noticed that with few exceptions the value of Pb/U increases as the uranium content decreases. This may be due to the possibility of the lead originally present in the magma having a gradually increasing relative importance as the lead generated from uranium decreases in amount. Thus it would seem in the case of nepheline and felspar that the lead so generated is of no importance whatever when compared with that originally present. Such minerals are, of course, valueless in age-estimations, and of the results given here only eight of the first nine will be used for determining the age. Omitting that of pyrochlore (1), since the single rather anomalous determination of lead could not be verified by a second estimation, these results give 0·046 as their mean, and if the uranium percentage be replaced by its approximate time-average the mean becomes 0·045. This gives an age of 370 million years, and is probably the most reliable estimate that can be deduced from the evidence.

5. *Summary of Analyses collected by Boltwood.**—(*a*) The analysis of five specimens of uraninite from Glastonbury (Conn.) gives a ratio of Pb/U = 0·041. The minerals occur in a pegmatite associated with a

* Boltwood, 'Am. Journ. Sci.,' 1907, p. 77.

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granite intruding Lower Carboniferous strata, and probably itself of Carboniferous age.

(*b*) Uraninite from Branchville (Conn.) gives four closely agreeing ratios, 0·053. The geological evidence here is similar to that at Glastonbury, with the exception that the intruded strata are of Silurian or Ordovician age.

(*c*) Material from dykes of pre-Carboniferous age in Carolina gives less consistent results, of which the mean ratio is 0·05.

(*d*) In Llano Co. (Texas), there occurs a group of metamorphosed sedimentary rocks of early Algonkian age. Into these the Burnet granites are intrusive, and are therefore somewhat younger than the schists and quartzites. The ratio of minerals from these igneous rocks is 0·160.

(*e*) Another group of minerals from Burnet Co. (Texas) and Douglas Co. (Colorado) gives a ratio of 0·175.

Geological evidence is similar to that of Llano Co., and it is impossible to say whether or not the rocks are older.

(*f*) The pre-Cambrian rocks of Sweden are divided by Högbom into three main divisions, Jotnian, Jatulian, and Archæan, in order of increasing age. Above the Archæan, but younger than the Jatulian, is a series of igneous massives known as the Sen-archæan granites, and with these are associated the famous uranium-bearing pegmatites of Scandinavia.

In a series of 17 minerals from these pegmatites, taken from all parts of Norway and Sweden, there appear to be two clearly marked groups. One gives a ratio of 0·125 and the other of 0·155. Amongst these rocks geological correlation is very speculative, but it is agreed that there is nothing by which any difference in age could be detected, and provisionally the two groups are regarded geologically as one.

(*g*) The greatest ratio is given by thorianite from Ceylon, for which $Pb/U = 0{\cdot}20$. Here the only evidence for the pre-Cambrian age of the minerals is derived from the similarity of the rocks to those of the fundamental complex of India. These latter underlie a vast series of sedimentary strata considered to be of pre-Cambrian age.

It should be observed that in calculating the above ratios U represents the time-average, and not the amount actually present. The difference is, however, not great.

6. *Conclusion.*—Evidence has been given to prove that the ratio Pb/U is nearly constant for minerals of the same age, the slight variability being what theoretically one would anticipate.

For minerals of increasing geological age the value of Pb/U also increases, as the following table clearly shows :—

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Geological period.	Pb/U.	Millions of years.
Carboniferous	0·041	340
Devonian	0·045	370
Pre-carboniferous	0·050	410
Silurian or Ordovician	0·053	430
Pre-Cambrian—		
a. Sweden	0·125	1025
	0·155	1270
b. United States	0·160	1310
	0·175	1435
c. Ceylon	0·20	1640

Wherever the geological evidence is clear, it is in agreement with that derived from lead as an index of age. Where it is obscure, as, for example, in connection with the pre-Cambrian rocks, to correlate which is an almost hopeless task, the evidence does not, at least, contradict the ages put forward. Indeed, it may confidently be hoped that this very method may in turn be applied to help the geologist in his most difficult task, that of unravelling the mystery of the oldest rocks of the earth's crust; and, further, it is to be hoped that by the careful study of igneous complexes, data will be collected from which it will be possible to graduate the geological column with an ever-increasingly accurate time scale.

In conclusion, I wish to express my thanks to those gentlemen who in any way have helped to make this investigation possible. I am indebted to Profs. Sir T. H. Holland, Brögger, and Högbom, and to the Director of the United States Geological Survey, for information regarding the geological position of many of the occurrences cited in §5; and to Dr. Prior for his permission to make preliminary electroscopic tests of several minerals in the collection of the Natural History Museum. Finally, I owe my best thanks to Prof. Strutt, at whose suggestion the work was attempted, for his ever-ready help and criticism, and for his kindness in obtaining for me the suite of minerals and allowing me the use of apparatus in their investigation.

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The Path of an Electron in Combined Radial Magnetic and Electric Fields.

By H. Stanley Allen, M.A., D.Sc., Senior Lecturer in Physics at University of London, King's College.

(Communicated by Sir Joseph Larmor, Sec. R.S. Received March 23,—Read May 11, 1911.)

1. In the course of an investigation with a focus tube, in which the anti-cathode was a magnetic pole, some interesting observations were made with regard to the distribution of the fluorescence on the walls of the tube as the magnetic field varied. In order to explain the changes observed, the path of an electron in a radial field was investigated mathematically, and was found to lie on a right circular cone whose vertex coincides with the magnetic pole. If the surface of the cone is developed into a plane the trace of the path is a conic section, with the vertex as focus. This result continues to hold when an electric field, with its lines of force radiating from the same point, is superposed on the magnetic field. Although the actual distribution of electric intensity in a highly exhausted tube* must differ widely from that here considered, the investigation sufficiently explains the facts observed.

Theoretical.

2. The object is to find the path of a particle of mass m carrying a charge e in combined magnetic and electric fields, when the lines of force are radial and are such as might be due to a single pole of strength μ coincident with an electric charge k.

The equations of motion of the particle are

$$\left.\begin{aligned} m\frac{d^2x}{dt^2} &= e\left(\frac{\mu y}{r^3}\frac{dz}{dt}-\frac{\mu z}{r^3}\frac{dy}{dt}+\frac{kx}{r^3}\right)\\ m\frac{d^2y}{dt^2} &= e\left(\frac{\mu z}{r^3}\frac{dx}{dt}-\frac{\mu x}{r^3}\frac{dz}{dt}+\frac{ky}{r^3}\right)\\ m\frac{d^2z}{dt^2} &= e\left(\frac{\mu x}{r^3}\frac{dy}{dt}-\frac{\mu y}{r^3}\frac{dx}{dt}+\frac{kz}{r^3}\right) \end{aligned}\right\} \qquad (1)$$

* F. W. Aston, 'Roy. Soc. Proc.,' January, 1911, vol. 84, pp. 526—535.

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If we multiply the second equation by z, the third equation by y, and subtract, we obtain on integration

$$z\frac{dy}{dt}-y\frac{dz}{dt}=\frac{\mu e}{m}\left(\frac{x}{r}-\mathrm{A}\right).$$

Similarly
$$x\frac{dz}{dt}-z\frac{dx}{dt}=\frac{\mu e}{m}\left(\frac{y}{r}-\mathrm{B}\right) \qquad (2)$$

and
$$y\frac{dx}{dt}-x\frac{dy}{dt}=\frac{\mu e}{m}\left(\frac{z}{r}-\mathrm{C}\right).$$

Multiply these equations by x, y, z, respectively and add.

Then
$$\mathrm{A}x+\mathrm{B}y+\mathrm{C}z=r, \qquad (3)$$

showing that the particle always lies on a right circular cone whose vertex is the origin.

3. It is easy to show from the equations of motion that the velocity V at a distance r from the origin is given by

$$\mathrm{V}^2-\mathrm{V}_0^2=\frac{2ke}{m}\left(\frac{1}{r_0}-\frac{1}{r}\right), \qquad (4)$$

where V_0, r_0, are the corresponding values for the point of projection. This is, in fact, the equation of energy.

If the particle is moving with velocity V in a direction making an angle β with a generating line OP of the cone, its acceleration along the normal is equal to $\mathrm{V}^2 \sin^2\beta/\mathrm{PG}$, while the force component in that direction is due to the action of magnetic field μ/r^2.

Hence
$$\frac{m\mathrm{V}^2\sin^2\beta}{\mathrm{PG}}=\frac{\mu}{r^2}e\mathrm{V}\sin\beta,$$

so that
$$\mathrm{V}r\sin\beta=\frac{\mu e}{m}\tan\alpha \qquad (5)$$

$$=\text{a constant, say } \mathrm{V}_0 r_0 \sin\beta_0.$$

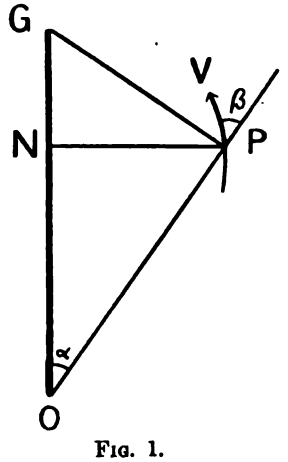

Fig. 1.

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Since $r \sin \beta = p$, the length of the perpendicular from the origin on the tangent to the orbit, this result may be written

$$\mathrm{V}p = \frac{\mu e}{m} \tan \alpha = \mathrm{V}_0 p_0. \qquad (6)$$

Thus, if the surface of the cone is developed into a plane, the velocity is that due to a central force ke/r^2, and $\mathrm{V}p$ is constant, so that the curve is a central orbit; it is therefore a conic section with the origin as focus.

If k and e have the same sign the force due to the electric field is one of repulsion, and the conic is an hyperbola. If k and e have opposite signs the force is an attraction and the curve is an hyperbola, an ellipse, or a parabola, according to the circumstances of projection.

The semi-axes of the conic are given by the relations

$$\pm a = \frac{ke}{m} \Big/ \left(\mathrm{V}_0^2 + \frac{2ke}{mr_0} \right), \quad \pm b^2 = \mathrm{V}_0^2 p_0^2 \Big/ \left(\mathrm{V}_0^2 + \frac{2ke}{mr_0} \right).$$

If $\mathrm{V}_0^2 = 2ke/mr_0$, the conic is a parabola whose latus rectum is $4p_0^2/r_0$.

4. Two particular cases merit special attention.

Case I. Motion of an Electron in a Radial Electric Field.—The surface of the cone becomes a plane.

Case II. Motion of an Electron in a Radial Magnetic Field.—The solution has been given by Poincaré.*

Putting $k = 0$ in the previous results we find that the velocity of the particle is constant, and that consequently $r \sin \beta$ or p is a constant. This implies that when the surface of the cone is developed into a plane the trace of the path is a straight line.

The number of times that the path on the cone overlaps itself depends on the value of the vertical angle ($2\pi/\sin \alpha$) of one sheet of the developed cone. If this angle is greater than π there is no point of overlapping, if its value be between π and $\frac{1}{2}\pi$ there is one such point, and if its value be between $\pi/2(n-1)$ and $\pi/2n$ there will be n such points, n being a positive integer.

5. *Numerical Estimates.*—It is instructive to consider the magnitude of the quantities determining the path of an electron ($e/m = 1{\cdot}7 \times 10^7$ E.M. units) projected with a velocity of 10^8 or 10^9 cm. per sec.

The value of the semi-angle α of the cone in certain cases is given in Table I :—

* 'Comptes Rendus,' 1896, vol. 123, pp. 530—533. [Sir Joseph Larmor has pointed out that the mathematically equivalent problem of finding the form assumed by a flexible string carrying an electric current in a radial magnetic field has been solved analytically by Darboux. The solution can be obtained directly by an application of the Principle of Least Action. See 'Proc. Lond. Math. Soc.,' 1884, vol. 15, pp. 158—170.]

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Table I.

	$V_0 = 10^8$ cm./sec.			$V_0 = 10^9$ cm./sec.		
	$\mu = 50.$	$\mu = 500.$	$\mu = 5000.$	$\mu = 50.$	$\mu = 500.$	$\mu = 5000.$
$p_0 = 1$ cm.	6° 43′	0° 40′	0° 4′	49° 38′	6° 43′	0° 40′
$p_0 = 2$ cm.	13° 45′	1° 21′	0° 8′	66° 58′	13° 45′	1° 21′

The strength of the radial electric field does not affect the angle of the cone, but determines the character of the developed path. Under the conditions met with in an ordinary focus tube the curve is an hyperbola differing but little from a straight line. Take, for example, the case in which $V_0 = 10^9$ cm./sec., $p_0 = 1$ cm., $r_0 = 6$ cm., and the electron is attracted towards the origin. In order to obtain a parabolic curve on the developed cone we should have to make $2ke/mr_0 = V_0^2$ by giving k a value of approximately 2×10^{11} *electromagnetic* units. By giving smaller values to k the curve becomes hyperbolic, and as k is diminished the semi-major axis a becomes small, the semi-minor axis b becomes nearly equal to p_0, and the distance from the focus (the vertex of the cone) to the vertex of the hyperbola approaches the same limit, p_0. In order to obtain an electric field whose strength at a few centimetres from the origin is measured in hundreds of volts per centimetre we have to assign extremely large values to k, but even then the developed path will not in general differ greatly from a straight line.

Experimental.

6. My attention was first drawn to the behaviour of the cathode stream in a radial magnetic field when using a focus tube of the form shown in fig. 2. The iron core of an electromagnet passed up through a barometer tube into the centre of the bulb, so that a strong magnetic pole could be produced at A. The form of the cathode C happened to be such that, when the bulb was highly exhausted, a ring of bright green fluorescence was seen on the glass at BB, encircling the iron bar. When the magnetic field was produced, this bright ring moved upwards till it reached a position such as DD. On gradually increasing the strength of the field, the bright ring rose higher to the position shown at EE. The lower part of the bulb was now practically free from luminosity. As the fluorescence on the wall of the bulb ascended, a violet cone of light made its appearance in the interior, the vertex of the cone being at the magnetic pole A. The boundary of the cone

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for a strong magnetic field is shown by the dotted lines AE. This luminous cone was visible also at higher pressures when there was no fluorescence on the glass walls.

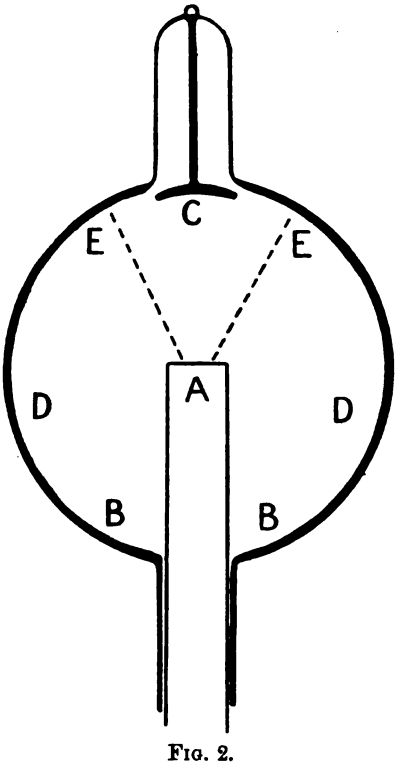

FIG. 2.

The explanation of these results by means of the theory already given is simple. The boundary of the violet cone seen in the bulb is the envelope of all the cones on which the spiral paths of the electrons lie. As the strength of the magnetic field is increased the vertical angles of these cones diminish, and consequently the angle of the enveloping cone also diminishes. The ring of fluorescence marks the curve in which the enveloping cone meets the glass of the bulb. As the field is increased the fluorescent ring gradually ascends the walls of the tube.

7. Experiments illustrating the behaviour of the cathode stream in a magnetic field due to a single pole have been carried out by Birkeland* and discussed by Poincaré.†

In order to illustrate further the case of Poincaré, in which no electric field acts on the particle, and the path is a geodesic line on a right circular cone, I

* 'Archives des Sciences' (Geneva), 1896, Ser. 4, vol. 1, pp. 407—512.

† *Loc. cit.*

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have experimented with vacuum tubes in which a fine pencil of cathode rays could be produced. A Wehnelt cathode was formed by melting a small speck of sealing-wax on a fine strip of platinum foil. When the foil was heated to a dull red heat by a current of 5 or 6 ampères, a potential difference of 100 or 200 volts was sufficient to maintain the discharge between the cathode and an aluminium anode placed in a side tube. The slow-moving stream of cathode particles was then subjected to the influence of one pole of a long electromagnet, and the path of the stream observed and photographed. In one tube the magnetic pole was situated in the centre of the spherical bulb through which the stream of electrons passed, in a second tube the pole was placed at any point outside the glass wall of the bulb. The strength of the pole could be increased up to about 1000 C.G.S. units. The spiral paths observed were found to lie on a cone, with its vertex at the magnetic pole.

In conclusion, I desire to express my thanks to Profs. C. G. Barkla and J. B. Dale for their interest in this work, and to the Government Grant Committee of the Royal Society for some of the apparatus employed.

On the Dynamical Nature of the Molecular Systems which emit Spectra of the Banded Type.

By Prof. E. T. Whittaker, Sc.D., F.R.S.

(Received March 24,—Read April 6, 1911.)

§ 1. *Summary of Paper.*—It is now widely believed, for the reasons recounted in § 2 below, that when the spectrum emitted by a luminous body is of the banded type, the small vibrators which give rise to the radiation are the molecules of the substance, as distinguished from atoms or ions. This result is applied in § 3, which constitutes the main body of the present paper, in order to suggest a dynamical system which is formed of two members in the same way as a diatomic molecule may be supposed to be formed of two atoms, and which has free periods of vibration related to each other by the same formula as holds in the case of banded spectra. This formula presents a certain peculiarity, in that the frequency of vibration occurs in it linearly; whereas in the equation for determining the free periods of dynamical systems in general, the frequency enters by its square. It is

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shown that from this peculiarity in the radiation of a molecule, certain inferences may be drawn regarding the dynamical character of the connection between the atoms within the molecule, namely, that the kinetic potential of a molecule consists of the kinetic potential of the atoms, together with certain gyroscopic terms: and it is suggested that the exchanges of heat in chemical reactions are due to the necessity for readjusting this gyroscopic energy when the molecules are altered.

In § 4 it is shown that a mechanism somewhat modified from that of § 3 would emit radiations connected by the same law as that which Balmer found for the hydrogen lines.

§ 2. *The Experimental Evidence regarding the Nature of the Vibrators.*—Those spectra which are known to belong to chemical compounds, as distinguished from the elements of which the compounds are composed, are generally of the banded type. This has suggested the hypothesis that banded spectra are produced by molecules, as distinguished from atoms; but as banded spectra are also in certain cases emitted by substances which are chemical elements, it is necessary to examine the question more closely. The elements bromine and iodine, for instance, when excited by a powerful electric discharge, emit spectra which are not banded, but emit banded spectra when the stimulus is less energetic. The banded spectrum may also be obtained reversed as an absorption spectrum, a fact which shows that it is produced by some agent which exists at ordinary temperatures and in the absence of electrical stimulation. These observations suggest that the non-banded spectrum belongs to the element in its most dissociated form, *e.g.*, the atom or ion—while the banded spectrum belongs to the molecular form; and further confirmation of this hypothesis is afforded by the fact that the banded spectrum of bromine vapour is extremely similar to the absorption-spectrum of iodine monochloride; it seems scarcely possible to doubt that, as the molecule I-Cl is the active agent in one case, the molecule Br-Br is the agent in the other. Still further confirmation is afforded by the observation that a temperature so high that the molecules Br_2 and I_2 are dissociated, the banded absorption-spectra are no longer obtained.

Observation of the banded spectra of other chemical elements leads to similar conclusions; thus Graham* has been able to distinguish between the absorption-spectrum of sulphur vapour in the form S_2 and that of the vapour in the form S_8.

On the whole, the evidence appears sufficient to justify an attempt to explain the mechanism of the production of banded spectra, on the assumption

* 'Roy. Soc. Proc.,' 1910, A, vol. 84, p. 311.

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that the vibrator emitting the radiation is a molecule formed by the combination of chemical atoms.*

§ 3. *A dynamical model of the molecule.*—Let us now attempt to design a dynamical model of the molecular vibrator.

The fact that so many properties of chemical substances are of the "additive atomic" kind, leads us to infer that atoms to a considerable extent retain their individuality when they are combined with one another to form molecules; so that a molecule is to be regarded not as a complete rearrangement of the electrons or other elements of which its atoms are composed, but rather as a system in which the atoms exist with comparatively little alteration of their internal structure, but with mutual connections such as may be expressed by additional terms or other modifications in the dynamical equations.

We shall therefore build up our dynamical model from two constituent systems representing the two atoms of a diatomic molecule. For simplicity we shall suppose these atoms to be alike, so that the molecule represented is that of a chemical element.

The position of any point within one of these constituent atoms may be specified by three generalised co-ordinates, which we shall denote by θ, ϕ, ψ. The state, at any instant, of the element of the atom which occupies the position (θ, ϕ, ψ) will be supposed to be specified by a variable u, so that u is a function of θ, ϕ, ψ, and the time t. It would be possible to extend this by assuming that two or three distinct variables u, v, w, are required to specify the state; the principles involved would be the same, and the subsequent analysis and results would be similar though more complicated.

We must now specify the distribution of potential energy within the atom. The simplest assumptions which can be made are that the potential energy of an element of the atom is composed of terms proportional to u^2, or to the squares or products of the first derivates of u with respect to θ, ϕ, or ψ, or to a sum of terms of this kind. That this is so may be seen by considering simple illustrative cases. For instance, suppose that this potential energy is really the electrostatic energy of the charges on a multitude of small conductors contained in the atom (each of these conductors being, say, connected to some other by a perfectly conducting wire having self-induction, so that the charges vary with the time); then it is known that the electro-

* A dynamical model for banded spectra was described by Sir Joseph Larmor in the article "Radiation" in the supplementary volumes (1902) of the tenth edition of the 'Encyclopædia Britannica.' In this the vibrating system is built up of a large number of constituents, and each line in the spectrum of a constituent gives rise to a band in the spectrum of the entire system.

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static energy of such a system is a quadratic function of the charges; and if we suppose that electrostatic induction is of sensible magnitude only between such conductors as are immediately adjacent to each other, the only terms in the energy which involve a particular charge e_r will be a quadratic combination of e_r, e_{r+i}, $e_{r+j}\ldots$, where e_{r+i}, $e_{r+j}\ldots$ denote the charges on conductors immediately adjacent to e_r. This quadratic combination may be written in the form

$$ae_r^2+b(e_r-e_{r+i})^2+c(e_r-e_{r+j})^2+\ldots,$$

and when we proceed to the limiting case in which the conductors are indefinitely small, indefinitely numerous, and indefinitely close together, and denote the density of charge in a volume-element by u, it is evident that the terms like ae_r^2 will give rise to a term in u^2, while the terms like $b(e_r-e_{r+i})^2$ will give rise to a quadratic function of the first derivates of u with respect to θ, ϕ, and ψ.

In any case, the occurrence of such terms as these in almost all the problems of the vibratory motion of continuous systems which have been investigated will be a sufficient justification for their introduction here.

We shall therefore assume that the potential energy resident in the element $d\theta\, d\phi\, d\psi$ of the first atom at the instant t is

$$\left\{\tfrac{1}{2}ku^2+\tfrac{1}{2}a\left(\frac{\partial u}{\partial\theta}\right)^2+\tfrac{1}{2}b\left(\frac{\partial u}{\partial\phi}\right)^2+\tfrac{1}{2}c\left(\frac{\partial u}{\partial\psi}\right)^2 +f\frac{\partial u}{\partial\phi}\frac{\partial u}{\partial\psi}+g\frac{\partial u}{\partial\psi}\frac{\partial u}{\partial\theta}+h\frac{\partial u}{\partial\theta}\frac{\partial u}{\partial\phi}\right\}d\theta\, d\phi\, d\psi.$$

In the most general case, the coefficients k, a, b, c, f, g, h, will be functions of θ, ϕ, ψ. We shall adopt the simplest supposition, which is that they are all constant.

The potential energy of an element of the second atom at the instant t will be represented by a similar expression. If (θ', ϕ', ψ') denote a system of generalised co-ordinates suitable for specifying position within the second atom, and if v denote a variable which specifies the state of the element $(d\theta', d\phi', d\psi')$ of this atom at the instant t, the potential energy of this element may be written

$$\left\{\tfrac{1}{2}kv^2+\tfrac{1}{2}a\left(\frac{\partial v}{\partial\theta'}\right)^2+\tfrac{1}{2}b\left(\frac{\partial v}{\partial\phi'}\right)^2+\tfrac{1}{2}c\left(\frac{\partial v}{\partial\psi'}\right)^2 +f\frac{\partial v}{\partial\phi'}\frac{\partial v}{\partial\psi'}+g\frac{\partial v}{\partial\psi'}\frac{\partial v}{\partial\theta'}+h\frac{\partial v}{\partial\theta'}\frac{\partial v}{\partial\phi'}\right\}d\theta'\, d\phi'\, d\psi'.$$

We have now to consider the nature of the connection between the two atoms. We shall suppose that the systems of generalised co-ordinates (θ, ϕ, ψ) and (θ', ϕ', ψ') are so chosen as to furnish the correlation between

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the interacting elements of the two atoms, *i.e.*, we shall suppose that the element (θ, ϕ, ψ) of one atom interacts with that element (θ', ϕ', ψ') of the other for which $\theta' = \theta$, $\phi' = \phi$, and $\psi' = \psi$; so that the connection between the atoms can be expressed in terms of the u and v which are functions of the same values of the arguments. We can therefore, in future, make one set of co-ordinates (θ, ϕ, ψ) do duty for both sets.

We may now arrange the permissible types of connections between the atoms in three classes (α), (β), (γ), as follows:—

(α) Such as may be expressed by adding to the kinetic potential terms of the types

$$uv, \quad \frac{\partial u}{\partial \theta}\frac{\partial v}{\partial \theta}, \quad \frac{\partial u}{\partial \phi}\frac{\partial v}{\partial \phi}, \quad \text{etc.},$$

which do not involve derivates with respect to the time. Terms of this kind would be introduced if, *e.g.*, we supposed that electrostatic induction takes place between the charges in one atom and the charges in the other.

(β) Such as may be expressed by adding to the kinetic potential or Lagrangian function terms of the types

$$\frac{\partial u}{\partial t}\frac{\partial v}{\partial t}, \quad \frac{\partial^2 u}{\partial t \partial \theta}\frac{\partial^2 v}{\partial t \partial \theta}, \quad \text{etc.},$$

which are products of a derivate of u with respect to the time (and possibly with respect to the co-ordinates also) by a similar derivate of v. Terms of this kind resemble those which represent the mutual induction of electric currents; they would be introduced if, *e.g.*, we supposed that electrokinetic induction takes place between the flux of charge in one atom and the flux of charge in the other.

(γ) Such as may be expressed by adding to the kinetic potential terms of the types

$$u\frac{\partial v}{\partial t}, \quad v\frac{\partial u}{\partial t}, \quad \frac{\partial u}{\partial \theta}\frac{\partial^2 v}{\partial t \partial \theta}, \quad \text{etc.},$$

in which one of the variables is differentiated with respect to the time and the other is not. Terms of this kind do not generally occur in the kinetic potential of a dynamical system when that function is first written down; but if the system contains "gyroscopic" or "ignorable" co-ordinates, and if these co-ordinates are removed by the process called "ignoration of co-ordinates," terms of this class may be introduced. To suppose that the connection between the two atoms is represented by such terms amounts, therefore, to supposing that the connection is effected by an intermediary agency of the gyroscopic type. It is to be remembered that gyrostatic energy may assume many different physical forms; for instance, an electric current flowing in a closed perfectly conducting circuit, which has self-induction, and also has

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mutual induction with other non-closed circuits in the system, would be represented by a gyroscopic co-ordinate; and, as Helmholtz showed, the fundamental equations of thermodynamics may be derived on the assumption that heat-energy may be represented by gyroscopic terms.

We have now to decide which of these three possible types of connection (α), (β), (γ), shall be adopted in our model molecule. Terms of the kind (α) and (β) represent the inductive influence which the atoms exert on each other in virtue of their propinquity, and we should naturally choose terms of this kind to represent the connection, if we were to regard a molecule as nothing more than two atoms which are so near as to exert strong mutual inductive influence. But, in spite of that persistency of certain atomic properties to which we have already referred, it is difficult to accept this as an adequate representation of the connection of the atoms in a molecule, when we recall the striking differences which a chemical compound frequently presents from the elements which compose it; and we are led to conclude that, while terms of the kinds (α) and (β) may and probably do exist, they do not represent the dominant feature in the internal economy of the molecule. There remains for consideration the type (γ). If terms of this type occur, the molecule must contain, in addition to the proper internal energy of the atoms, a certain amount of energy of the gyroscopic type, peculiar to the combined or molecular state. That this is the case we may, however, readily believe, for chemical changes, *i.e.*, rearrangements and exchanges of the atoms between molecules, are in general attended by the evolution or absorption of heat; and it seems natural to think of this as the balance left over after the redistribution of gyroscopic energy in the molecules. This idea is further sustained by a closer examination; for connecting terms of the type (γ) in the kinetic potential do not furnish any contribution to the energy, although they influence the motion (just as, *e.g.*, an external magnetic field does not influence the energy of a moving electron, although it causes a deviation of its motion), and the energy of the molecular system therefore consists of the sum of the internal energies of the atoms, together with a constant part, which represents the energy of the gyroscopic connection.

It will be felt to be an argument in favour of this assumption of gyroscopic energy, that it confers a definite individuality on the molecule without destroying the individuality of the atoms of which it is composed, thus enabling us to account at the same time for the persistence of certain properties which are characteristic of the atom, and the appearance of other properties which are characteristic of the molecule.

It may be further remarked that this conception accounts for a polarity of molecules, even of the molecules of chemical elements, such as is

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suggested by the phenomena of crystals, without assuming that atoms of the same element are different from each other; for such a term as $u\partial v/\partial t$ is unsymmetrical with respect to the two atoms, this term being, in fact, equivalent to $-v\partial u/\partial t$.* The polarity of the molecule is thus represented as a consequence of the connection of the two atoms within it by a gyrostatic link.

Assuming, then, that the connection between the two atoms is represented by a gyrostatic term $lu\,\partial v/\partial t$, and that the inertia of the atoms does not play any important part in the modes of vibration that are to be studied, so that it may be neglected, the kinetic potential of the entire molecule may be represented in the form

$$\begin{aligned}\mathrm{L} = \iiint d\theta\, d\phi\, d\psi \Big\{ &\tfrac{1}{2}ku^2 + \tfrac{1}{2}a\left(\frac{\partial u}{\partial\theta}\right)^2 + \tfrac{1}{2}b\left(\frac{\partial u}{\partial\phi}\right)^2 + \tfrac{1}{2}c\left(\frac{\partial u}{\partial\psi}\right)^2 \\ &+ f\frac{\partial u}{\partial\phi}\frac{\partial u}{\partial\psi} + g\frac{\partial u}{\partial\psi}\frac{\partial u}{\partial\theta} + h\frac{\partial u}{\partial\theta}\frac{\partial u}{\partial\phi} + \tfrac{1}{2}kv^2 + \tfrac{1}{2}a\left(\frac{\partial v}{\partial\theta}\right)^2 + \tfrac{1}{2}b\left(\frac{\partial v}{\partial\phi}\right)^2 + \tfrac{1}{2}c\left(\frac{\partial v}{\partial\psi}\right)^2 \\ &+ f\frac{\partial v}{\partial\phi}\frac{\partial v}{\partial\psi} + g\frac{\partial v}{\partial\psi}\frac{\partial v}{\partial\theta} + h\frac{\partial v}{\partial\theta}\frac{\partial v}{\partial\phi} + lu\frac{\partial v}{\partial t}\Big\},\end{aligned}$$

where k, a, b, c, f, g, h, l denote constants.

The variational equation is

$$\delta\int \mathrm{L}\,dt = 0.$$

Writing this equation *in extenso*, performing the variational operation on each of its terms, integrating by parts so as to obtain δu or δv in each term free from differentiations, and then equating to zero the coefficients of δu and δv in the resulting integrand, we obtain the equations of motion

$$ku - a\frac{\partial^2 u}{\partial\theta^2} - b\frac{\partial^2 u}{\partial\phi^2} - c\frac{\partial^2 u}{\partial\psi^2} - 2f\frac{\partial^2 u}{\partial\phi\,\partial\psi} - 2g\frac{\partial^2 u}{\partial\psi\,\partial\theta} - 2h\frac{\partial^2 u}{\partial\theta\,\partial\phi} + l\frac{\partial v}{\partial t} = 0,$$

$$kv - a\frac{\partial^2 v}{\partial\theta^2} - b\frac{\partial^2 v}{\partial\phi^2} - c\frac{\partial^2 v}{\partial\psi^2} - 2f\frac{\partial^2 v}{\partial\phi\,\partial\psi} - 2g\frac{\partial^2 v}{\partial\psi\,\partial\theta} - 2h\frac{\partial^2 v}{\partial\theta\,\partial\phi} - l\frac{\partial u}{\partial t} = 0.$$

These equations must now be integrated, subject to the boundary conditions. Regarding the latter, the elementary theory of the vibrations of rods, membranes, etc., familiarises us with two kinds of boundary conditions; namely, those exemplified by the vibrations of a straight rod of finite length, in which case there are conditions at the two ends, and those exemplified in the vibrations of an endless rod having a circular

* For the combination $u\frac{\partial v}{\partial t} + v\frac{\partial}{\partial t}$ in the kinetic potential, being a perfect differential with respect to t, would furnish no terms in the equations of motion, and therefore $u\partial v/\partial t$ is equivalent to $-v\partial u/\partial t$.

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form, in which case the condition is that the same physical conditions are to be repeated when the azimuth is increased by 2π. So far as the frequencies of free vibration are concerned, however, these two kinds of boundary-conditions lead ultimately to much the same kind of equation; the latter kind are somewhat simpler, as they require the introduction of fewer symbols; we shall, therefore, take the boundary-conditions in our problem to be of this character, so as to require the solutions of the equations of motion to be periodic functions of θ, ϕ, and ψ, of period 2π. A typical normal oscillation of the system will therefore be represented by the equations

$$u = \mathrm{A}\sin(nt+p\theta+q\phi+r\psi),$$
$$v = \mathrm{B}\cos(nt+p\theta+q\phi+r\psi),$$

where p, q, r, are integers, and n denotes the frequency.

Substituting these values of u and v in the equations of motion, we have

$$ln\mathrm{B} = (k+ap^2+bq^2+cr^2+2fqr+2grp+2hpq)\,\mathrm{A},$$
$$ln\mathrm{A} = (k+ap^2+bq^2+cr^2+2fqr+2grp+2hpq)\,\mathrm{B}.$$

Eliminating A and B, we have

$$\pm n = k+ap^2+bq^2+cr^2+2fqr+2grp+2hpq,$$

where p, q, r can assume in succession all integer values.

This equation determines the frequency n of the free vibrations of the molecule.

Now according to Deslandres' formula for the frequencies of vibration in a banded spectrum, the frequency of the pth line in the qth band in the rth family of bands is

$$n = p^2f(q^2,r^2)+\mathrm{B}q^2+\phi(r^2).$$

This formula of Deslandres may evidently be derived from our analysis if we suppose that the product-terms in the potential energy which have the coefficients f, g, h, are zero, and moreover that the potential energy contains higher derivates such as $\partial^2u/\partial\theta^2\times\partial^2u/\partial\phi^2$, $(\partial^4u/\partial\phi^4)^2$, etc.; in such assumptions there is nothing unnatural.

Some writers do not accept Deslandres' formula, asserting that the banded spectra are better represented if terms involving the first and other odd powers of p, q, r, are included in the empirical formula. If so, the terms in f, g, h, above should be retained. The equation, in fact, has a considerable adaptability consistent with the retention of its cardinal feature, which is that the frequency (*not* the square of the frequency, which is the quantity usually occurring in such equations derived from dynamical systems) is expressed as a simple function of three quantities, p, q, r, which are to assume in succession all integer values. This cardinal feature of the

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frequency-equation is derived from the cardinal feature of the model, which is the union of two atoms within a molecule by a connection of the gyrostatic type.

§ 4. *The Series Spectrum of Hydrogen.*—It may be not without interest to add that it is possible on these principles to construct a vibrator whose free periods are those of the series spectrum of hydrogen.

We have only to postulate two similar constituents in the vibrator, the potential energy of the one being

$$\tfrac{1}{2}au^2+\tfrac{1}{2}b\left(\frac{\partial u}{\partial\theta}\right)^2,$$

and of the other being

$$\tfrac{1}{2}av^2+\tfrac{1}{2}b\left(\frac{\partial v}{\partial\theta}\right)^2,$$

the two constituents being joined by a connection of the gyroscopic type, which after ignoration gives rise to a term

$$\frac{\partial u}{\partial\theta}\frac{\partial^2 v}{\partial t\,\partial\theta}$$

in the kinetic potential. This resembles the term introduced in the case of the banded spectra, differing from it only in that the derivates $\partial u/\partial\theta$ and $\partial v/\partial\theta$ replace u and v. The variational equation is now

$$0=\delta\iint dt\,d\theta\left\{\tfrac{1}{2}au^2+\tfrac{1}{2}b\left(\frac{\partial u}{\partial\theta}\right)^2+\tfrac{1}{2}av^2+\tfrac{1}{2}b\left(\frac{\partial v}{\partial\theta}\right)^2+\frac{\partial u}{\partial\theta}\frac{\partial^2 v}{\partial t\,\partial\theta}\right\},$$

which gives the equations of motion

$$au-b\frac{\partial^2 u}{\partial\theta^2}-\frac{\partial^3 v}{\partial t\,\partial\theta^2}=0,$$

$$av-b\frac{\partial^2 v}{\partial\theta^2}+\frac{\partial^3 u}{\partial t\,\partial\theta^2}=0.$$

We assume that each constituent is ring-shaped, so that it returns into itself when θ increases by 2π. A normal free oscillation will therefore be represented by

$$u=\mathrm{A}\sin(nt+m\theta),$$

$$v=\mathrm{B}\cos(nt+m\theta),$$

where m denotes an integer and n denotes the frequency of vibration. Substituting these values in the equations of motion, we have

$$(a+m^2b)\,\mathrm{A}=m^2n\mathrm{B},$$

$$(a+m^2b)\,\mathrm{B}=m^2n\mathrm{A},$$

so the equation which determines the frequencies of vibration is

$$\pm n=b+\frac{a}{m^2},$$

as in the hydrogen spectrum.

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On some Mineral Constituents of a Dusty Atmosphere.

By W. N. Hartley, D.Sc., F.R.S., Royal College of Science, Dublin.

(Received April 4,—Read May 11, 1911.)

During the past 12 months I have had occasion to ascertain the nature of the mineral constituents of an ordinarily turbid atmosphere. By means of a small portable quartz spectrograph several series of spark spectra were photographed with graduated exposures of 1, 5, 10, 20, 40, and 60 seconds, all on the same plate. The electrodes in the first series were cadmium, iron, nickel, and copper, a self-induction coil being interposed to eliminate the air spectrum and the short metallic lines.

Several plates taken from only the cadmium electrodes exhibited features of particular interest when minutely examined. Though the spectra are small, the instrument gives fine definition from the red potassium line about λ 7665·6 to that of cadmium λ 2194·7.

With Wratten and Wainwright's panchromatic plates, an exposure of one second renders all the principal lines of cadmium, including $\lambda\lambda$ 4800 and 2265, with 10 seconds all the rays from λ 6438 are obtained. The solar spectrum from *b* to M is faintly visible at all exposures from 1 to 60 seconds inclusive.

The conspicuous H and K lines seen in the first three exposures have their usual appearance; but, on the third spectrum, exposed 20 seconds, the K line has, at its exact centre, an extremely narrow sharp black line; in succeeding exposures this line becomes longer and intensified.

With 40 seconds' exposure a similar black line is just discernible on H, and it is stronger with 60 seconds. Other parts of the solar spectrum are overlaid by exceedingly fine dark lines which it was proved do not belong to the cadmium spectrum, but were caused by solid matter in suspension in the atmosphere being vaporised by the spark. The dark lines on H and K are easily explained by the presence of calcium carbonate in very minute particles of dust suspended in the air. I have called attention to this in former publications.* It was proved in these experiments that the lines did not originate from impurities in the metallic cadmium, because the same electrodes with longer exposures yielded spectra without any impurity lines, when the sparks were passed in an atmosphere of hydrogen. It was also found that whether in the open air, or in a quiet room near a window, the most prominent lines of calcium were always present.

* Hartley, 'Phil. Trans.,' 1884, Part I, pp. 49—62, and Part II, pp. 325—342. Also 'British Association Report, Aberdeen,' 1885, and 'Journ. Soc. Arts,' 1886, pp. 396—415.

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A line, rather more refrangible than G, was carefully measured, and proved to be that of calcium, λ 4226·9; it is the *ultimate* line of the element in oxyhydrogen flame spectra.

There are two lines just on either side of M; there is no doubt that these are the calcium lines λλ 3737·2 and 3706·3.

It has been shown by Hartley and Adeney's wave-length determinations* that the line of cadmium measured by Mascart (No. 12) is a triple line, the components being distinguished by the following letters and wave-lengths:— α 3261·2, β 3252·6, and γ 3250·5. With a self-induction coil the β line disappears. On examining plates photographed on three successive days, with exposures varying from 1 to 60 seconds, it was seen that two plates showed only two lines α and γ. The third plate showed, at an exposure of one second, an extremely fine and very sharp black line, more refrangible than the other two, which, by very careful measurements, was proved to be the ultimate line of copper, λ 3274. With five seconds' exposure this and all other succeeding spectra on the plate showed another line less refrangible than the cadmium group, which was proved to be the penultimate line of copper, λ 3247·7.

A comparison of the plates of spectra showed that with the same exposures on each succeeding day the five lines of calcium and the two lines of copper became stronger; in other words, the increased strength of the lines showed that the outside air became more dusty. This was seen to be actually the case, under the conditions of a dry atmosphere and a hot sun continuing for six or seven days in the month of May.

To ascertain the origin of the copper was an enquiry attended with some difficulty, the quantity diffused in the atmosphere of the city being comparatively large.

Copper has been proved to be a constituent of coal ashes, and of the flue-dust from gasworks and chemical works, of soot, and of dust from the clouds in hail, snow, and sleet.† These sources, however, contain other constituents, notably lead, nickel, and iron.

The constant traffic of tram-cars and motor-cars in the street raised dust, which caused an increased haziness of the atmosphere day by day, and corresponding increase in the number and intensity of the calcium lines in the spectra.

While making these observations, the prevalence of copper in the dust was accounted for by the repeated flashes on the overhead cable, which is in the centre of a wide street (St. Stephen's Green) at a distance of 54 feet from the

* 'Phil. Trans.' 1884, Part I.

† Hartley and Ramage, 'Roy. Soc. Proc.,' 1901, vol. 68, p. 97.

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window of my private room. The condensation of the vapour of copper after each discharge must yield a dust of extreme tenuity such as could not arise from mechanical action, such as scraping or abrasion of the solid metal.

The lines identified from their proximity to, or coincidence with, solar lines, are as follows; the wave-lengths of calcium are taken from Eder and Valenta's spark lines:—

	λ	λ	
Near G	4308	4226·9	Calcium.
H, K	Coincident	3968·6, 3933·3	Calcium.
Near M	3727	3737·2, 3706·2	Calcium.
Near Q	3284·7	3274·0, 3247·7	Copper.

Of seven plates of spectra photographed in the months of April and May two were very carefully measured with the micrometer. Twenty-two lines were positively identified with those of elements known to be contained in atmospheric dust. The lines are principally the ultimate lines of the respective elements.

The following is a list of the wave-lengths found and the wave-lengths adopted:—

Wave-lengths found.	Wave-lengths adopted.	Origin of lines.
4227·5	4226·9	Calcium.*
4058·5	4057·8	Lead.*
3965·5	3968·6	Calcium.*
3932·5	3933·8	
3878·0	3876·2	Carbon.
3870·0	3871·2	
3733·0	3735·0	Iron.*
Very faint.		
3683·5	3683·1	Lead.*
3643	3639·7	
Very faint.		
3495	3496	Manganese.
3484·5	3483	
3416	3415	Nickel.*
3274·8	3274·0	Copper.*
3247·9	3247·7	
2802·1	2802·4	Magnesium.*
2794·5	2794·5	
2614·5	2614·8	Lead.
2594·0	2594·0	Manganese.*
2575·0	2576·2	
2480·0	2478·7†	Carbon.*

* Ultimate lines.

† A. de Gramont, 'Comptes Rendus,' 1908, vol. 146, p. 1260. This line appears distinctly with an exposure of 60 seconds, but as a short line. Of the other two lines one corresponds with λ 3876·5, Liveing and Dewar, the other with 3871·5, Kayser and Runge, and 3872, Eder and Valenta, the second edge of the cyanogen band No. 3. See 'Proc. Roy. Soc.,' 1896, vol. 60, p. 216. The first edge 3883·8 is obscured by a nitrogen band.

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Spectra were photographed from portions of the same cadmium electrodes, six months later, in a part of the college as far removed from the frontage as possible, close to a large garden, and with no street thoroughfare within 100 yards.

There had been heavy rain, which had washed out much of the dust from the air. Notwithstanding, the wave-length measurements of two feeble strange lines identified them with copper, and the five calcium lines were very distinct.

Spectra were photographed from cadmium electrodes in hydrogen with exposures of one, two, three, and four minutes; cadmium in air exposed one minute. The spectrum taken in the hydrogen atmosphere, and exposed *four* minutes, was in all respects of similar intensity to that taken in air in *one* minute, except beyond λ 2418·5, where the continuous rays between the lines commenced to fade away. The spectra taken in hydrogen showed no trace whatever of the lines of either copper or calcium, and many other feeble lines were entirely absent which undoubtedly are representative of the other constituents of atmospheric dust. It is thus proved, absolutely, that the copper and calcium were the constituents of dust diffused through the atmosphere of the city.

Determinations of the weight of material necessary to give the lines of these spectra in the manner described, and with such short exposures, have been completed. From the loss of weight of the dry electrodes by the passage of the spark during successive intervals of 10 minutes, the weight of metallic calcium volatilised in one minute, and in one second, was calculated. The number of spark discharges per second was accurately determined, and likewise the number of discharges necessary to render the lines of calcium, as photographed from atmospheric dust, with an exposure of 60 seconds. Similarly with copper, the number of discharges necessary to render the *ultimate* line and the two lines respectively, as measured on plates exposed to atmospheric dust for one second and for five seconds, was ascertained, and the weight of copper volatilised at each spark discharge was accurately determined. It was found that, in order to render the five principal lines in the spectrum of calcium, the weight of the metal passing between the electrodes in 60 seconds was from 0·0001 to 0·00014 mgrm., or, as calcium carbonate, from 0·00025 to 0·00035 mgrm. Similarly, the quantity of copper which passed between the electrodes in one second was from 0·0005 to 0·0007 mgrm., and in five seconds from 0·001 to 0·0014 mgrm. These quantities yield the spectra photographed, and the proportion of copper in the dust thus appears to be 10 times as great as that of the calcium.

Both the calcium and copper reactions in the spark are more delicate than

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the sodium test by the yellow flame, or even by the photography of the *ultimate* lines of sodium in the oxyhydrogen flame and spark. Metallic sodium renders no lines with one spark when photographed, and with five sparks the lines λ 3301·1 and λ 3302·5 are both stronger than the yellow lines (mean λ 5893·2). These lines do not appear on any of the cadmium plates.

The reactions of lead, manganese, and magnesium in the spark are much more sensitive than those of sodium, calcium, or copper. For instance, 0·00003 mgrm. of manganese is volatilised by one spark discharge, and yields a spectrum with the following *ultimate group* of lines: 2949·3, 2939·4, and 2933·1.

As no atmosphere is free from dust, and that of cities is particularly dusty, these mineral constituents must be regarded as possible reagents in cases where there is evidence that very minute quantities of basic substances can initiate chemical reactions and isodynamic changes, such as have generally been considered as spontaneous, and in all cases where a solution in contact with air is liable to be affected.

On the Absolute Measurement of Light: A Proposal for an Ultimate Light Standard.

By R. A. Houstoun, M.A., Ph.D., D.Sc., Lecturer in Physical Optics in the University of Glasgow.

(Communicated by Prof. Andrew Gray, F.R.S. Received April 5,—Read May 11, 1911.)

The measurement of the intensity of a source of light is, it is well known, a somewhat unsatisfactory process. The eye cannot estimate light intensity; it can only tell when the illumination of two adjacent surfaces is equal. If, for example, we desire to measure the intensity of a metal filament lamp, we compare it with a Hefner lamp and say that the intensities are inversely as the squares of the distances from the photometer head, when equal illumination is obtained. In strictness, however, this method is applicable only when the colours of the two sources, or more accurately when the distribution of energy in the spectra of the two sources, is exactly the same; for the relative luminosity of the different colours of a spectrum varies with the intensity of that spectrum. Abney has two well-known curves illustrating

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this.* One, which represents the relative luminosity of the different colours of a spectrum at ordinary intensity, has a maximum in the orange; the other, which is for a spectrum with the same distribution of energy, but with an intensity of less than 1/100 candle-foot, has its maximum in the green. If, therefore, we have an extremely long photometer bench, and an experimenter with normal colour vision compares the intensities of the metal filament lamp and the Hefner lamp, at first placing the Hefner lamp one foot from the photometer head and afterwards placing it more than 100 ft. from the latter, he should not obtain the same result both times. In the first case, owing to the reddish tint of the Hefner lamp, the intensity of the metal filament lamp should appear less. If, again, a second observer, whose colour vision is slightly abnormal, compares the lamps at the first distance, he gets a third result.

Of course the difficulty does not arise in practice, because the sources to be compared have usually the same colour and the illumination of the field of the photometer does not vary over a wide range. Still, a standard unit of light should meet all conceivable cases, and we are at present unable to state satisfactorily in terms of our standards, once for all, the candle power of, for example, a mercury vapour lamp. In order to be definite we must specify, first of all, normal colour vision on the part of the observer, and then we must state the illumination of the fields he compares. It is, of course, the Purkinje effect, the change from rod to cone vision, that causes all this trouble. And it is precisely within the range of illumination in common use, 1 to 100 metre-candles, that this change from rod to cone vision takes place.

I think it is now possible to place the photometry of different coloured lights on an exact footing, at least as far as ultimate measurements are concerned, by removing it out of the field of physiology altogether into the field of electricity, which is a much more exact science.

Why can we not measure candle power by means of a thermopile? Simply because the thermopile measures the total energy radiated, irrespective of wave-length. The energy of every radiation receives the same value. Now infra-red and ultra-violet radiations produce no effect at all on the eye, and the light-producing effect of the same quantity of energy is much greater in the middle of the spectrum than at its ends. If we place in front of the thermopile a light filter which has the property of stopping entirely all the infra-red and ultra-violet radiation and of cutting down the energy of the visible spectrum in inverse ratio to its light-producing effect, that is, *if we weight each radiation according to its visibility*, then the deflections will be proportional to the light received. This combination of filter and

* 'Colour Vision,' p. 103.

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thermopile is then a kind of electric eye, which has a property that the human eye has not, namely, the property of registering the intensity of the light to which it is exposed.*

The relative visibility of light of different wave-lengths for different intensities of that light has as yet been determined only for one eye, namely, that of Prof. A. König, and the results are given in a very convenient table in a paper by P. G. Nutting.†

Prof. König's colour vision was normal, and so in default of other data we can take this table as applying to the average human eye.

In choosing a filter we must fix on something capable of accurate reproduction. This rules coloured glasses out of the question, unless they are made under standard conditions. We are therefore restricted to liquids in glass cells. Commercial dyes of ill-defined composition are subject to the same objection as coloured glasses. Solutions of salts which can be varied in strength give us more latitude, and are therefore to be preferred to liquids of a fixed composition. A series of researches on the absorption of light by aqueous solutions of inorganic salts in the ultra-violet, visible spectrum, and infra-red is now being carried out in the Physical Laboratory of the University of Glasgow, as a result of which I am in possession of a considerable amount of data not at present accessible to others, and from it I have no hesitation in concluding that the most suitable filter is a 3 cm. thickness of copper sulphate in water of concentration 0·200 gramme-molecule per litre, followed by a 1 cm. thickness of potassium bichromate of concentration 0·0025 gramme-molecule per litre. I have examined eight

* After writing this paper my attention was called to the fact that an attempt to put this method into practice has already been made by Ch. Féry ("Photométrie à lecture directe: Rendement optique de quelques luminaires," 'Journ. de Phys.,' 1908, vol. 4, p. 638). He used a solution of copper acetate in water with a radiomicrometer, and has selected the same total thickness of water as myself, namely, 4 cm. He has not, however, gone into the matter fully, and does not give the fraction transmitted by his filter throughout any part of the spectrum. Copper acetate alone cannot give the proper absorption in the violet. I have also used a radiomicrometer, and my experience is that it is inferior in sensitiveness to the apparatus described in this paper, although possessing the advantages of simplicity and cheapness.

J. E. Petavel, in a well-known paper ("A Preliminary Study for a New Standard of Light," 'Electrician,' 1902–3, vol. 50, p. 1012), proposes to let the radiation from incandescent platinum fall upon two thermopiles, one with a glass filter and the other with a filter of "black fluorspar" in front of it, and to use the ratio of the deflections as a means of determining the temperature of the platinum. The brightness of the latter as measured by a photometer at a definite temperature is to be the standard. His work is thus altogether on different lines. Black fluorspar seems to me altogether too indefinite a substance for his purpose.

† "The Luminous Equivalent of Radiation," 'Bull. Bureau of Standards,' 1908, vol. 5, p. 279.

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different kinds of commercial coloured glass, but none of them is of the least use for the purpose, owing to not stopping the near infra-red.

The absorption of light in aqueous solutions of inorganic salts obeys the following equation,

$$I = I_0 . 10^{-Acd},$$

which also defines A, the molecular extinction coefficient of the salt for the wave-length considered. I_0 is the initial intensity of the light, I its intensity after passing through a thickness d of solution, d being measured in centimetres, and c is the concentration of the solution in gramme-molecules per litre. We may take A as independent of c except for wide ranges and at particular points in some spectra.

The following tables give the values of A for the two salts in question in the ultra-violet and for the copper sulphate in the infra-red. The values

Infra-red.

λ.	A. $CuSO_4,5H_2O$. $c = 0{\cdot}03435$.	λ.	A. $CuSO_4,5H_2O$. $c = 0{\cdot}03435$.
μ.		μ.	
0·684	6·36	0·910	9·1
0·720	9·8	0·980	7·1
0·750	11·5	1·07	5·8
0·794	11·7	1·17	4·1
0·850	11·1	1·27	3·0

Ultra-violet.

$CuSO_4,5H_2O$.			$K_2Cr_2O_7$.		
c.	λ.	A.	c.	λ.	A.
	μ.			μ.	
0·01	0·267	52·0	0·0001	0·241	7160
0·03	0·278	34·0	—	0·269	11100
0·05	0·282	20·2	—	0·284	7440
—	0·287	13·0	—	0·291	5070
0·10	0·291	10·1	—	0·300	2720
—	0·292	8·6	0·0005	0·308	2320
—	0·296	6·5	0·0003	? 0·316	2080
0·30	0·299	3·37	0·0005	0·325	2320
—	0·309	1·48	0·0001	0·331	2720
—	0·313	0·78	—	0·336	5070
—	? 0·322	0·08	—	0·349	7440
			—	? 0·375	10000
			—	0·397	7440
			0·0003	0·410	3080
			0·001	0·416	1030

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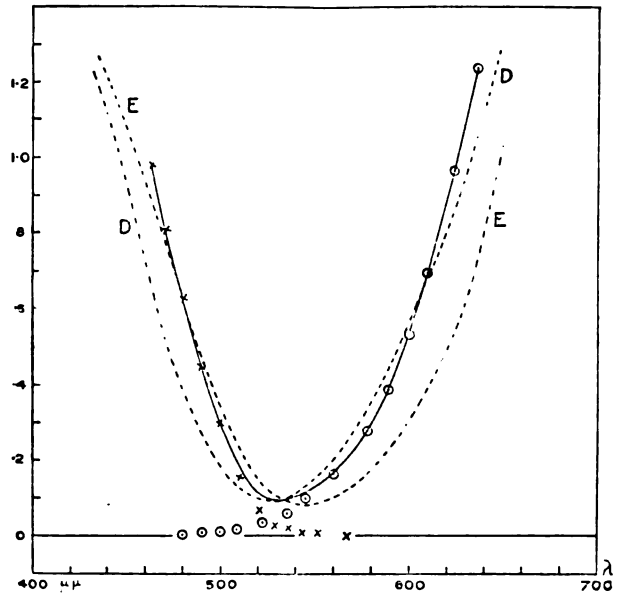
for the visible spectrum have already been determined by Grünbaum* and by A. S. Russell and the author.† The values for copper sulphate in the infra-red were obtained with a linear thermopile, the source of light being a Nernst glower. The values for the ultra-violet were obtained by means of a quartz photometer of original design which has recently been worked out by John S. Anderson and the author, and a description of which is already in course of publication. It is, of course, impossible to give values further into the infra-red owing to the absorption of water. At the strength and thickness used in the filter potassium bichromate does not exercise any appreciable absorption in the infra-red.

The values of A_{cd} for the two filters have been calculated from the tables and are shown in the following diagram. The values for copper sulphate are shown by ⊙'s and the values for potassium bichromate by ×'s; Grünbaum's values are taken for the copper sulphate and our own for the potassium bichromate. The smooth curve is the sum of the ordinates for each salt. The logarithms of the columns D and E in Nutting's table were then calculated, their sign was changed, and they were plotted on the diagram as the dotted curves. In order to facilitate comparison with the smooth curve, the vertical scale for the dotted curves is displaced 0·08 up. Of course, we can add any constant quantity to the ordinates of the smooth curve without altering the relative absorption of the different colours.



* 'Ann. d. Phys.,' (4) 1903, vol. 12, p. 1004.

† 'Roy. Soc. Edin. Proc.,' 1908–9, vol. 29, p. 69.

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On the one side the smooth curve agrees with E, on the other side with D. D is for an illumination of 2·30 metre-candles and E for an illumination of 9·22 metre-candles. We are therefore justified in assuming that our filters weight the radiation of the visible spectrum correctly according to its visibility to normal colour vision, the illumination of the field being about 6 metre-candles. If we take as our standard another illumination of the field, it is easy to shift the minimum of the curve by diminishing the concentration of the copper sulphate and increasing the concentration of the potassium bichromate or *vice versâ*. The strength of the copper sulphate, however, cannot be weakened much unless an additional thickness of water or of, say, ferrous ammonium sulphate is used, otherwise there will not be a sufficient margin of safety in the infra-red. Aqueous solutions of ferrous ammonium sulphate are, it is now known, very effective in stopping heat rays while allowing the light rays to pass.* They are much more efficient than alum, which in this respect is no better than water.

If we neglect the light absorbed in the glass, the fraction of light transmitted by our filter is equal to

$$10^{-0\cdot6A_C} \times 10^{-0\cdot0025A_K} \times k,$$

where A_C is the molecular extinction coefficient of the copper sulphate, A_K is the molecular extinction coefficient of the potassium bichromate, and k the fraction that would be transmitted by 4 cm. of pure water alone. In order that the effect due to the different constituents of the filter may be seen, I have calculated $10^{-0\cdot6A_C}$, $10^{-0\cdot0025A_K}$, and k throughout the spectrum, using for k the values of E. Aschkinass.† The results are given in the second, third, and fourth columns of the following table. The product of the three factors, that is, the transmissivity of the whole filter, is given in the fifth column.

Of course, in addition to the above, the absorption of the glass of the cells has to be considered. Glass absorbs all radiations below 0·330 μ and above 3·00 μ.

The filter is weakest in the infra-red at 1·27 μ. In the normal energy spectra of our ordinary light sources the ordinates at 1·27 μ are about twenty times or thereabouts the ordinates at 0·5 μ. With the strength used, the stopping power of the filter is hence ample, but this point in the spectrum must be watched if the concentration of the copper sulphate is diminished much.

Having found by calculation that the radiation received by a thermopile

* R. A. Houstoun and J. Logie, 'Phys. Zs.,' vol. 11, p. 672.

† 'Wied. Ann.,' 1895, vol. 55, p. 401.

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λ.	$10^{-0\cdot6 A_C}$.	$10^{-0\cdot0025 A_K}$.	k.	$10^{-0\cdot6 A_C} \times 10^{-0\cdot0025 A_K} \times k$.
μ.				
0·227 }	$<6\cdot31\ 10^{-11}$	$<1\cdot3\ 10^{-18}$	0·99 }	$<8\ 10^{-29}$
0·241 }		$1\cdot3\ 10^{-18}$	0·99 }	
0·284	$6\cdot31\ 10^{-11}$	$2\cdot5\ 10^{-19}$	0·99	$1\cdot6\ 10^{-29}$
0·300	$1\cdot20\ 10^{-2}$	$1\cdot6\ 10^{-7}$	1·00	$1\cdot9\ 10^{-9}$
0·308	0·107	$1\cdot6\ 10^{-6}$	—	$1\cdot7\ 10^{-7}$
0·325	0·89	$1\cdot6\ 10^{-6}$	—	$1\cdot5\ 10^{-7}$
0·336		$1\cdot9\ 10^{-13}$	—	$<1\cdot9\ 10^{-13}$
0·397		$2\cdot5\ 10^{-19}$	—	$<2\cdot5\ 10^{-19}$
0·416		$2\cdot6\ 10^{-3}$	—	$<2\cdot6\ 10^{-3}$
0·463 }	<0·986	0·105	—	<0·105
0·471 }		0·158	—	<0·158
0·480	0·986	0·234	—	0·229
0·489	0·977	0·355	—	0·347
0·499	0·968	0·501	—	0·485
0·5086	0·951	0·661	—	0·63
0·5461	0·792	0·982	—	0·77
0·5780	0·521	1·00	—	0·52
0·6004	0·292	—	0·99	0·29
0·6239	0·108	—	0·99	0·107
0·6452	0·0336	—	0·99	0·034
0·684	$1\cdot54\ 10^{-4}$	—	0·99	$1\cdot53\ 10^{-4}$
0·720	$1\cdot32\ 10^{-6}$	—	0·95	$1\cdot25\ 10^{-6}$
0·750	$1\cdot26\ 10^{-7}$	—	0·91	$1\cdot14\ 10^{-7}$
0·794	$9\cdot55\ 10^{-8}$	—	0·92	$8\cdot8\ 10^{-8}$
0·850	$2\cdot2\ 10^{-7}$	—	0·86	$1\cdot9\ 10^{-7}$
0·910	$3\cdot5\ 10^{-6}$	—	0·73	$2\cdot5\ 10^{-6}$
0·980	$5\cdot5\ 10^{-5}$	—	0·20	$1\cdot5\ 10^{-5}$
1·09	$3\cdot3\ 10^{-4}$	—	0·48	$1\cdot6\ 10^{-4}$
1·17	$3\cdot5\ 10^{-3}$	—	0·054	$1\cdot9\ 10^{-4}$
1·27	$1\cdot6\ 10^{-2}$	—	0·0085	$1\cdot3\ 10^{-4}$
1·40			$2\ 10^{-41}$	$<2\ 10^{-41}$
			Never $>10^{-18}$ all the way to 8·5 μ.	

through this filter should be proportional to the light incident on the filter, I proceeded by direct experiment to determine if this actually was the case. I had three thermopiles at my disposal, a Rubens linear one with iron-constantan couples and two older ones, of different types, but both with antimony-bismuth couples. The Rubens thermopile consists of 20 couples on a length of 2 cm., the wires being soldered together with silver beads, which are flattened into discs of 1 mm. diameter. Hence its receiving area is about 0·157 sq. cm. In the case of each of the other two, the receiving area was about 1 square inch, and the number of couples was greater, yet the Rubens thermopile was as sensitive, even without its reflectors, reached the steady state in a shorter time, and had a very much steadier zero. Only the Rubens thermopile was used.

The galvanometer was a Du Bois Rubens ironclad one, of resistance 10 ohms, the property of the Carnegie Trust for the Universities of Scotland.

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In order to protect it from vibration, it was suspended from a bracket in the wall by three wires each about 1½ metres long, and hung with its three levelling screws clearing the table by about 1 cm. Between the table and levelling screws loose wads of cotton wool were placed for the purpose of damping any vibrations that might arise. The lamp and scale were 1½ metres from the mirror. The resistance of the thermopile was 5 ohms. At the sensitiveness used, the period was 3 seconds and ½ mm. on the scale indicated a current of 10^{-9} ampères.

It soon became evident that this high sensitiveness was to be fully utilised. When the thermopile was set up at a distance of 33 cm. from a 32 c.p. carbon glow lamp with the filters in front, the deflection was only 17 ½-mm. When this lamp is run at its marked voltage, 250 volts, about 2·6 per cent. of its total radiation is light, that is, lies between 0·400 μ and 0·760 μ, but only a fraction of this 2·6 per cent. gets through the filter. Perhaps altogether about 1/1000 of the total radiation passes through the filter.

The thermopile was, then, set up at a distance of 33 cm. from the 32 c.p. carbon glow lamp with the filters in front, the $K_2Cr_2O_7$ filter being next the thermopile. On the other side of the lamp was a photometer bench, at the other end of which there was a 125 volt tantalum lamp that was run off a storage battery. The carbon lamp and the tantalum lamp were compared by a wedge photometer. When this comparison was being made the tantalum lamp was always shunted by a current balance and constant resistance, the latter being chosen so that the open part of the scale of the balance was in use, and from the indications of the balance the voltage on the tantalum lamp could be kept constant to 1/800 by means of a rheostat. At the voltage used the horizontal candle power of the tantalum lamp, measured by a Hefner lamp, was 7·13 British candles.

Readings were then taken for different voltages alternately with the thermopile and with the photometer. One set of results is given in the following table and plotted in the following curve.

Test of a 32-candle power Glow Lamp.

Voltage.	Galvanometer readings.						Photometer readings.				
	Throws.					Mean.	Individual settings.				Candle power.
207·1	5·5	4·0	4·0	3·0	4·5	4·2	117·5	114·5	112·5	114·5	6·15
222·5	8·0	7·0	6·5	6·7		7·0	96·5	98·5	96·5	98·5	11·2
251·6	18·0	16·0	17·5	18·0		17·4	77·5	76·5	76·5	76·5	24·9
283·7	38·0	38·0	36·5	36·5		37·2	59·5	57·5	59·5	58·5	53·8
304·7	56·5	56·5	60·0	59·8		58·2	48·5	47·5	49·5	49·5	88·1

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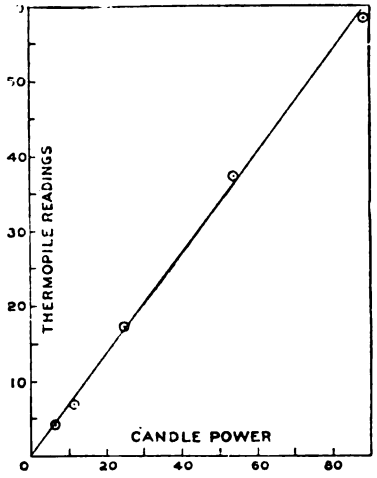

Every reading taken is given. At each voltage two readings were first taken with the thermopile, then two settings of the photometer were made; the remaining thermopile readings were then made, and, finally, the last two photometer readings were taken. The numbers given in the table as photometer settings are the distances of the wedge in centimetres from the comparison lamp. The total distance between the two lamps was 220 cm.

The curve should, of course, be a straight line. The agreement is very good when we consider that the galvanometer readings are $\frac{1}{2}$ mm. at $1\frac{1}{2}$ metres distance from the mirror, and that for the last point the photometer was getting rather near the comparison lamp for the inverse square law to hold.

I have altered the strength of the $K_2Cr_2O_7$ to $c = 0{\cdot}0125$ and of the $CuSO_4,5H_2O$ to $c = 0{\cdot}350$, and the proportionality still holds.

A thermopile used with such a filter can therefore be employed for measuring candle power, more especially mean spherical candle power, because it is only necessary to set up equally sensitive thermopiles over the sphere and to connect them in series with the one galvanometer. All difficulties connected with the integration thus vanish. The method works also quite as well in broad daylight as in a darkened room, the deflections being the same in each case. I think, however, that it is not suitable for commercial application, on account of the high sensitiveness of the galvanometer required. Its importance lies in the fact that it can be used for defining our unit of light and for providing a satisfactory basis on which lights of different colour can be compared, irrespective of intensity and of idiosyncrasy on the part of the observer.

The amount of light lost by reflection at the glass surfaces and by

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absorption in the glass of the cells can be easily determined by filling the cells with water and using a spectrophotometer to determine the fraction of the incident light transmitted. It is sensibly the same throughout the visible spectrum, and has the value 0·84 for both of the cells employed. It is easy to determine what the galvanometer deflections would have been, had there been no reflection losses or absorption losses in the glass; we have only to multiply by $1/(0{\cdot}84)^2$. In determining the distance of the thermopile from the source of light, we have, of course, to multiply each thickness of glass and liquid traversed by its index of refraction. I propose therefore to define the unit of light intensity as follows :—

The unit of light intensity is that source the total intensity of radiation from which at an optical distance of 1 metre after passing through an ideal filter would be x ergs/cm.^{2} sec., the ideal filter to be one possessing the light absorbing properties of a 3 cm. thick aqueous solution of $CuSO_4,5H_2O$ of strength 0·200 gramme-molecules per litre and a 1 cm. thick aqueous solution of $K_2Cr_2O_7$ of strength0 ·0025 gramme-molecules per litre, but neither to reflect nor to absorb any light in any other way.

I think it better to eliminate the properties of the glass in this way. Different cells have quite an appreciable difference in absorption and the transmission coefficient of a cell is easy to determine. The definition, has the advantage of connecting up light closer with the C.G.S. system. By means of his pyrheliometer K. Ångström* has been able to measure the radiation from terrestrial sources to less than 1 per cent., the chief difficulty being to allow for want of "absolute blackness" on the part of the receiving surface. The radiation-receiving surface in my experiments was about 0·157 sq. cm., and the distance from the source 33 cms. By increasing the light-receiving area and using Ångström's method it should be possible to determine x with sufficient accuracy. For the standard candle in the units specified it is roughly 0·8.

* 'Astrophys. Journ.,' 1899, vol. 9, p. 332; 'Phys. Rev.,' 1893, vol. 1, p. 365.

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On a Method of making Visible the Paths of Ionising Particles through a Gas.

By C. T. R. Wilson, M.A., F.R.S.

(Received April 19,—Read May 11, 1911.)

[Plate 9.]

The tracks of individual α- or β-particles, or of ionising rays of any kind, through a moist gas may be made visible by condensing water upon the ions set free, a suitable form of expansion apparatus being used for the purpose.

In order that the clouds formed should give a true picture of the trails of ions left by the ionising particles, it is necessary that little or no stirring up of the gas should result from the expansion. It is desirable that no interval long enough to allow of appreciable diffusion of the ions should elapse between their liberation and the production of the super-saturation necessary for the condensation of water upon them; and that the cloud-chamber should be free from all ions other than those in the freshly formed trails.

The apparatus which has proved effective for the purpose differs from that used in my former experiments on condensation nuclei mainly in the form of the cloud-chamber. This is cylindrical, with flat horizontal roof and floors, its diameter being 7·5 cm., and its height between 4 and 5 mm. before expansion, and about 6·2 mm. after expansion. The expansion is effected by the sudden downward displacement of the floor of the cloud-chamber; this is constituted by the flat top of a hollow brass piston open below, and set in motion by the method described in former papers.

The clouds are viewed through the roof of the cloud-chamber, which is of glass, coated below with a uniform layer of clear gelatine. The floor is also covered by a layer of gelatine, in this case blackened by the addition of a little Indian ink.

Besides serving as a cement to attach the glass roof of the cloud-chamber, the gelatine lining avoids altogether one of the principal sources of trouble in all cloud experiments—the deposition of dew on the inner surface of the glass. In addition it forms, when moist, a conducting layer which may be maintained at a constant potential; the connection with a source of potential being made through an annular strip of tinfoil fixed by means of the gelatine round the margin of the glass plate which forms the roof, and extending to just within the cylindrical glass wall of the cloud-chamber.

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The potential difference applied between the roof and floor, in the observations described below, amounted to 8 volts. Any ions set free before an expansion were thus exposed to a field of about 16 volts per centimetre, and had at the most about $\frac{1}{2}$ cm. to travel. The only ions "caught," on expansion, were thus those which had been produced within less than 1/40th of a second before the expansion, and such as were set free in the short interval after the expansion during which the super-saturation exceeded the limit necessary for condensation upon the ions.

A horizontal stratum of the air in the cloud-chamber was illuminated by a suitable source and condensing lens; for eye observations a Nernst lamp is a convenient source. For the purpose of photographing the clouds a Leyden jar discharge through mercury vapour at atmospheric pressure was employed, the mercury being contained in a horizontal capillary quartz tube, of which the central portion was heated to vaporise the mercury. The spark was fired by the mechanism which started the expansion, and took place one- or two-tenths of a second later. The camera was inclined at an angle of 30° to the horizontal, the distances being arranged to give a picture of approximately the natural size, and the photographic plate being tilted so that the whole illuminated layer might be approximately in focus.

Results.

Clouds with Large Expansions.—The clouds formed with large expansions in the absence of ions ($v_2/v_1 > 1{\cdot}38$) showed, so far as the eye could judge, a uniform distribution of drops.

Ionisation by α-Rays.—The radium-tipped metal tongue from a spinthariscope was placed inside the cloud-chamber, and the effect of expansion observed after removal of the dust particles. The cloud condensed on the ions, while varying infinitely in detail, was always of the same general character as that of which fig. 1 (Plate 9) is a photograph. The photograph gives, however, but a poor idea of the really beautiful appearance of these clouds. It must be remembered, in interpreting the photographs, that trails of all ages, up to about 1/40th of a second, may be present, the most sharply defined being those left by particles which have traversed the air while super-saturated to the extent required to cause condensation upon the ions. The trail of ions produced by a particle which traversed the gas before the expansion may have had time to divide into a positively and a negatively charged portion under the action of the electric field, and in each of these a certain amount of diffusion of the ions may have taken place before expansion. It is possible, therefore, that the few remarkably sharply defined lines, about 1/10 mm. wide, alone represent the actual

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FIG. 1.

Cloud formed on Ions due to α-Rays.

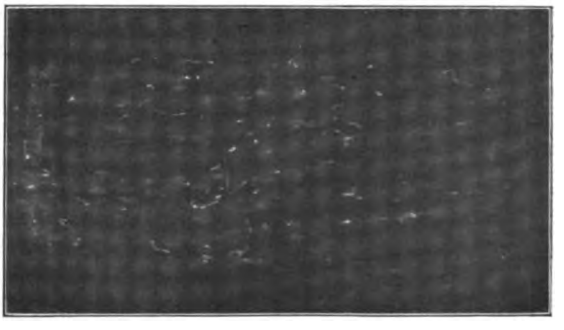

FIG. 2.

Cloud formed on Ions due to X-Rays.

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distribution of ions immediately after the passage of the α-particles, before any appreciable diffusion has had time to take place.

Ionisation by β-Rays.—A small quantity of impure radium salt in a thin glass bulb was held against a small aperture, closed by aluminium weighing about 1 mgrm. per sq. cm., in the cylindrical vertical wall of the cloud-chamber. On making an expansion sufficient to catch all the ions, two or three absolutely straight thread-like lines of cloud were generally seen radiating across the vessel from the aperture. In addition, other similar lines were occasionally seen crossing the vessel in other directions, probably secondary β-rays from the walls of the vessel.

Ionisation by γ-Rays.—The γ-rays from 30 mgrm. of radium bromide, placed at a distance of 30 cm. on the same horizontal level as the cloud-chamber, produced on expansion a cloud entirely localised in streaks and patches and consisting mainly of fine, perfectly straight threads, traversing the vessel in all directions—the tracks of β-particles from the walls of the vessel.

Ionisation by X-Rays.—When the air is allowed to expand while exposed to the radiation from an X-ray bulb the whole of the region traversed by the primary beam is seen to be filled with minute streaks and patches of cloud, a few due to secondary X-rays appearing also outside the primary beam. A photograph shows the cloudlets to be mainly small thread-like objects not more than a few millimetres in length, and many of them being considerably less than 1/10 mm. in breadth. Few of them are straight, some of them showing complete loops. Many of them show a peculiar beaded structure. In addition to the thread-like cloudlets, there are minute patches of cloud which may be merely foreshortened threads. Other fainter and more diffuse patches and streaks are also present, possibly representing older trails, in which the ions have had time to diffuse considerably before the expansion.

The droplets composing the threads have been deposited on the ions produced along the paths of the actually effective ionising rays. These are probably of the nature of easily absorbed secondary β- or cathode-rays; some doubtless starting from the roof or floor of the cloud-chamber, others, however (the larger number when a limited horizontal beam of X-rays is used), originating in the gas. The results are in agreement with Bragg's view that the whole of the ionisation by X-rays may be regarded as being due to β- or cathode-rays arising from the X-rays.

The question whether the original X-radiation has a continuous wave front, or is itself corpuscular as Bragg supposes, or has in some other way its energy localised around definite points in the manner suggested by

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Sir J. J. Thomson, remains undecided. The method already furnishes, however, a very direct proof that when ionisation by X-rays occurs corpuscles are liberated, each with energy sufficient to enable it to produce a large number of ions along its course.

The few preliminary photographs which have been taken were not obtained under conditions suitable for an examination of the relation of the initial direction of the cathode rays produced in the air to that of the incident Röntgen radiation. I hope shortly to obtain photographs which will admit of this being done.

The Vacuum Tube Spectra of Mercury.

By Frank Horton, D.Sc., M.A., Fellow of St. John's College, Cambridge.

(Communicated by Sir J. J. Thomson, F.R.S. Received April 26,— Read May 25, 1911.)

The 'Proceedings of the Royal Society' for 1860 contain a paper by Plücker,* which gives an account of the first observations of the spectrum of the luminous discharge through mercury vapour at a low pressure. Plücker used a vacuum tube with mercury electrodes, and he observed and made measurements of the wave-lengths of ten lines. A few years later, working with Hittorf,† he found that the mercury spectrum may be obtained more brightly when a Leyden jar and spark gap are used in parallel with the tube. Other conditions affecting the lines observed in the vacuum tube spectrum of mercury have since been recorded by various investigators; for instance, the widening of the lines with increased pressure was observed by Ciamician,‡ and the effect of the presence of different gases in the vacuum tube on the brightness of the mercury lines was investigated by Sundell,§ who found that the mercury lines were visible when the tube contained hydrogen at considerable pressures, but that with oxygen or nitrogen they could only be seen when the pressure was very low.

The spectrum of the light from the mercury arc was first investigated by Liveing and Dewar,‖ and afterwards very completely by Kayser and

* Plücker, 'Roy. Soc. Proc.,' 1860, vol. 10, p. 256.
† Plücker and Hittorf, 'Phil. Trans.,' 1865, vol. 155, p. 1.
‡ Ciamician, 'Wien. Ber.,' 1878, vol. 78, p. 867.
§ Sundell, 'Phil. Mag.' [5], 1887, vol. 24, p. 98.
‖ Liveing and Dewar, 'Phil. Trans.,' 1883, vol. 174, p. 187.

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Runge,* but the first thorough investigation of the spectrum of mercury in vacuum tubes was that of Eder and Valenta,† published in 1894. These observers found that the lines obtained from a vacuum tube at low pressures were much sharper than those given by the arc or spark. The number of lines obtained depended on the current density and on the temperature of the vapour. The spectrum richest in lines was obtained by having one part of the vacuum tube hot and the rest cold, so that the mercury distilled through the capillary. Using a Leyden jar they were then able to measure a great many new lines. From the wider parts of the vacuum tube they obtained a banded spectrum, but this (which was first observed by them) was seen best in the capillary when the discharge was passed without a Leyden jar. Introducing capacity into the circuit had the effect of breaking up these bands into an immense number of fine lines—the "rich line spectrum"—some 670 lines are recorded in their paper.

The observations of Eder and Valenta have since been confirmed by Huff.‡ As the result of a detailed study of the effects of capacity, self-induction, and temperature on the spectrum, he came to the conclusion that, by suitably regulating the temperature of the tube and the conditions of the discharge, the spectrum could be made to change gradually from that consisting of bands to that richest in lines. A background of continuous spectrum was obtained, especially when capacity was placed in the circuit and strong discharges were passed at rather high temperatures.

A thorough investigation of the spectrum of mercury has also been made by Stark,§ who came to the conclusion that mercury possesses two distinct line spectra, viz., that given by an arc *in vacuo*, and that given by a vacuum tube discharge. The lines obtained in the arc spectrum were those previously observed by Kayser and Runge, together with a few others of small intensity. Those obtained in the spectrum of the glow discharge Stark compares with the "rich line spectrum" of Eder and Valenta. The latter observers give more lines in the less refrangible part of the spectrum, but Stark records many more in the ultra-violet. The spectrum given by the mercury arc light is called by Stark the first line spectrum of mercury, that given by the glow discharge is the second line spectrum. He puts forward the hypothesis that the first line spectrum is due to monovalent, and the second line spectrum to divalent mercury atoms—atoms which have lost respectively one and two negative corpuscles.

* Kayser and Runge, 'Wied. Ann.,' 1891, vol. 43, p. 384.
† Eder and Valenta, 'Denkschr. Wien. Akad.,' 1894, vol. 61, p. 401.
‡ Huff, 'Astrophys. Journ.,' 1900, vol. 12, p. 103.
§ Stark, 'Ann. d. Phys.,' 1905, vol. 16, p. 490.

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A very complete investigation of the vacuum tube spectrum of mercury has been made by Stiles,* who gave particular attention to the red end, a region of the spectrum which has not been so closely investigated as those which more readily affect a photographic plate. While investigating the discharge of electricity for a hot lime cathode in a vacuum tube, the author† was struck by the appearance of five sharp, bright lines in the red and orange regions of the spectrum, lines which could not be found recorded in any of the ordinary tables of wave-lengths, although two of them agreed roughly with faint lines observed by Stark in the vacuum tube spectrum of mercury. It now appears that these lines had been previously observed and measured by Hermann‡ in the arc spectrum of mercury. They have since been measured by Stiles and their wave-lengths recorded in the paper already referred to.

These lines are so sharp and bright in the spectrum of the discharge from a hot lime cathode through mercury vapour, that I was tempted to investigate the spectrum of the discharge in an ordinary vacuum tube under different electrical conditions. It was found that under certain conditions several new red and orange lines could be obtained. These appeared when a condenser was used, and the discharge was sent through the vapour at a low pressure. I therefore tried the effect of varying the pressure of the vapour through which the discharge from a hot lime cathode passed, in order to see if a different spectrum could be obtained. The discharge tube used was of the form figured in my previous paper, except that the platinum anode was covered with mercury. The amount of vapour present in the tube could be varied by warming or cooling it. When the lime cathode was heated and a discharge from a battery of cells passed through the tube, the five red and orange lines were seen quite brilliantly, the other bright lines observed being the two yellow lines 5791, 5770, the green 5461, the blue 4916, and the violet 4359. On increasing the vapour pressure by warming the mercury, all the lines became wider and blurred and, with the exception of the wave-lengths just mentioned, they finally became indistinguishable in a brilliant background of continuous spectrum. On reducing the pressure of the vapour by cooling the tube in liquid air, the whole spectrum became very faint and finally disappeared as the luminosity ceased, the lines in the red and orange regions being the first to go.

It thus appears that the normal spectrum produced by the lime cathode discharge through mercury vapour contains these five red and orange lines

* Stiles, 'Astrophys. Journ.,' 1909, vol. 30, p. 48.

† Horton, 'Camb. Phil. Soc. Proc.,' 1908, vol. 14, p. 501.

‡ Hermann, 'Ann. d. Phys.,' 1905, vol. 16, p. 684.

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in addition to the other bright ones mentioned above; a few faint lines are also visible—the complete spectrum is given in Column II of the table on p. 295. As will be seen in the following pages, this spectrum can also be obtained, under certain conditions, from the induction coil discharge through an ordinary vacuum tube.

The Preparation of the Vacuum Tubes.

In the investigations of the spectrum of the induction coil discharge through mercury vapour the vacuum tubes employed were of the shape indicated in the accompanying diagrams:—

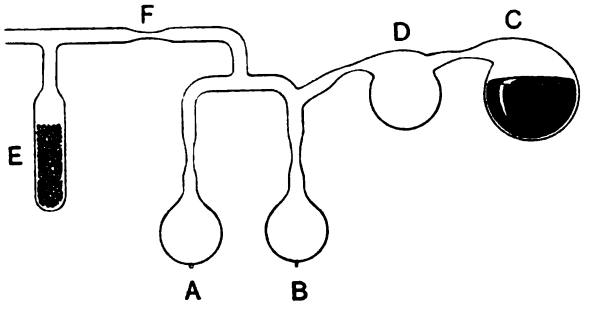

Fig. 1.

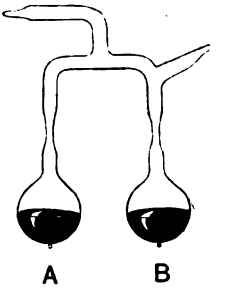

Fig. 2.

Fig. 1 shows the tube before being filled with mercury; fig. 2 shows it sealed off from the pump and ready for use. The bulbs A and B containing the mercury were each about 2 cm. in diameter. The capillaries were about 2 mm. wide, but differed slightly in width in the different tubes used.

The method of getting the mercury into the vacuum tube in a high state of purity may be gathered from fig. 1. The glass tubing used to make the apparatus there shown was most carefully cleaned with chromic acid, and when complete the apparatus was cleaned out with boiling nitric acid, and finally with distilled water. Boiling nitric acid in the bulbs A and B served to remove hydrogen from the small platinum electrodes fused into them. After careful drying, the discharge tube AB with the bulb D was sealed on to a mercury pump with a phosphorus pentoxide drying tube and the tube E containing cocoanut charcoal in connection. The large bulb C was carefully cleaned, dried, and nearly filled with purified mercury. It was then sealed on to the bulb D as shown in the diagram. The whole apparatus was exhausted as completely as possible by means of the mercury pump, the evacuation being finally completed by cooling the carbon tube E in liquid air. The tube AB and the bulb D were then heated all over by means of a blow-pipe flame to remove gas occluded on the inside surface of the glass.

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The heating was continued for half an hour or more, and the glass was made so hot that in places it softened and sank in on account of the vacuum inside. The bulb C was then very gently warmed by means of a small flame placed about 20 cm. below it, and the mercury began to distil over and to collect in the bulb D. When about two-thirds of the mercury in C had distilled into D the small connecting tube was fused up by a blow-pipe flame, and C was removed from the apparatus. D was then gently warmed, and two-thirds of the mercury in it was distilled over into the discharge tube AB. D was then sealed off and removed. The mercury in the bulbs A and B was heated, and a discharge from an induction coil was passed through the tube. After this had been going on for some time the temperature of the discharge tube was considerably raised by gentle heating with a blow-pipe flame, and a quantity of the mercury distilled over into the tubes leading to the pump and collected there and in the tube E, which, throughout these operations, remained in a vessel of liquid air. Finally the connecting tube was melted at F, where previously it had been drawn down, and the discharge tube was separated from the pump and was ready for use (fig. 2). In this manner tubes could be prepared containing mercury only, all traces of foreign substances being completely excluded. At the ordinary room temperature the vacuum in the tube was so complete that no discharge could be sent through it by a large Marconi coil giving a 10-inch spark.

In one of the tubes used the mercury was prepared from pure mercuric oxide supplied by Kahlbaum. This was decomposed by heating it in a vacuum, the oxygen being continually pumped away. The mercury was distilled into the discharge tube in the manner already described. All the tubes used gave similar spectra, but in one or two of them the carbon monoxide band spectrum was sometimes seen after they had been in use for some weeks, and, strangely enough, generally when the pressure of mercury vapour in the tube was rather high. I think that this gas came from the glass of the discharge tube, for the inner surface of the bulbs A and B at the level of the mercury became broken up by the passage of the discharge, and this might lead to a liberation of CO_2 (which gives the band spectrum) from carbonates used in the manufacture of the glass. This would account for the spectrum appearing when the pressure of the mercury vapour was high, for then the tube was being most strongly heated. However, I have one tube, made over two years ago, which has never shown anything but mercury lines.

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The Spectroscope, etc.

The spectroscope used to measure the wave-lengths of the lines was one of Hilger's direct wave-length reading instruments. This was very carefully calibrated by means of a helium-hydrogen-mercury tube. It was further calibrated in the red, orange, and yellow, by means of a neon tube. A curve of corrections was plotted showing the correction to be applied to any reading when the instrument was adjusted so that the reading of the mercury orange line, 6152, was correct.

The mercury vacuum tube under observation was held in a wooden stand, and under each of the bulbs A and B, but some 20 cm. below them, was placed a small flame which could be adjusted in size. The coil used to produce the discharge was a large Marconi instrument, taking 3 to 12 ampères through the primary, and capable of giving a 10-inch spark in the secondary circuit.

When extra capacity was required in the circuit, two large Leyden jars of gallon size, joined in parallel, were included. This was done by lessening the size of a spark gap until sparks passed between the knobs, or sometimes by screwing these knobs up together. It was found that the two jars in parallel had more effect on the spectrum than one jar alone, and the effect was not noticeably increased by using six jars. The appearance of the spectrum varied greatly with the size and nature of the spark between the knobs in the Leyden jar circuit, the spectrum with most lines being observed when sharp, bright, intermittent sparks passed.

Experimental Results.

In the experiments with the mercury vacuum tubes described in this paper, several spectra were obtained which appeared to be produced by quite definite conditions. These spectra contained, in some cases, the same lines, but with different relative intensities. Each spectrum was quite distinct and easily recognisable, and could be made to appear on arranging the electrical conditions known to produce it. The methods of obtaining the different spectra will now be described.

The simplest spectrum is that which I have called the five-line spectrum of mercury, consisting of the yellow pair 5791, 5770, the green 5461, the blue 4916, and the violet line 4359. This spectrum is always obtained when both limbs of the tube are fairly hot and the discharge is running easily, the interrupter of the induction coil working quietly and without much sparking. Under these circumstances, even with the knobs of the spark gap in connection with the Leyden jars close together, no spark (or a very small and quiet one) passes between them, and screwing them together until they touch

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causes no difference in the spectrum of the discharge. During these observations, mercury condenses and collects in the upper, horizontal part of the tube. This suddenly runs over into one or other of the limbs of the tube, and some of it falls down into the mercury in the bulb, but generally a blob remains, blocking up a portion of the capillary. This immediately changes the nature of the discharge; sparks are heard between the knobs of the spark gap, and usually the induction coil works more noisily. Instead of the simple five-line spectrum, the lines recorded in column II of Table I appear. This spectrum is the one given by the discharge from a glowing lime cathode through mercury vapour, and its characteristic feature is that the three orange lines 6235, 6124, 6074, are present and are equally bright.

During this experiment both bulbs, A and B, fig. 2, have been gently warmed. If, now, the flame under bulb A is turned out, so that the temperature of that limb of the tube falls and the mercury distils over from B to A, and if the tube is then gently tapped with the finger so that a blob of mercury is made to collect in one of the capillaries, at the instant the blob forms the luminosity of the tube increases, and the spectrum observed is that given in column III of Table I. The most noticeable features of this are the presence of the mercury orange line 6152, and that, of the other three orange lines, which in Spectrum II are equally bright, 6235 is now brighter than 6124 or 6074. The order of luminosity of the two red lines is now reversed, and many more lines appear in the more refrangible parts of the spectrum. On the other hand, the two faint, but sharp, lines 5352, 5319, of Spectrum II are now no longer seen. In this experiment the mercury vapour is at a fairly high pressure, though, of course, not at quite so high a pressure as in the first experiment, in which both bulbs were heated. The spectrum obtained before the blob appears in the tube is the five-line spectrum, and, as before, this is not altered by putting the capacity in the circuit by screwing up the spark gap. Spectrum III is given by the light from either capillary after the blob has formed in one of them. There is a lot of continuous spectrum as a background to these lines; this disappears when the blob falls out of the capillary, and the five-line spectrum then becomes very bright again. The other lines generally persist faintly for a short time, but they soon disappear. This seems to indicate that the systems emitting them are no longer being produced in the vapour, but that those which existed at the moment the blob fell out of the capillary are not immediately destroyed when the electrical conditions are changed. The formation of the blob of mercury in the capillary has the effect of making the tube "harder"; for the two fresh surfaces of mercury formed across the tube act as an extra

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Table I.

I.		II.		III.		IV.		V.	
Five-line spectrum.	Intensity.	Spectrum of glowing lime discharge.	Intensity.		Intensity.		Intensity.	Lines measured by Eder and Valenta.	Intensity.
		6908	1	6908	3				
		6717	4	6717	2				
		6235	8	6235	8				
				6152	8	6152	8	6152	9
		6124	8	6124	5				
		6074	8	6074	5				
				5890	6	5890	3	5889	4
				5873	2	5873	3	5872	6
				5819	1			5819	1
				5806	2			5804	1
5791	9	5791	8	5791	8	5791	8	5791	10
5770	9	5770	8	5770	8	5770	8	5770	10
						5728	1*s*	5728*	5
		5679	1	5679	4	5679	6	5679	8
						5596	2*s*	5596	6
5461	10	5461	10	5461	10	5461	10	5461	10
				5427	1*s*	5427	8	5427	8
				5409	1				
				5366	6			5366	4
				5356	1			5356*	1
		5352	1*s*					5352*	1
		5319	1*s*						
						5207	1*b*	5207	4
						5128	1*b*		
				5047	3			5047	1
				4960	4	4960	1*b*	4960	6
4916	4	4916	4	4916	6	4916	1*b*	4916	4
						4797	1*b*	4797	2
4359	10	4359	6	4359	8	4359	8	4359	10

The lines of Eder and Valenta marked with an asterisk were only observed in the many lined spectrum.
b signifies that the line was blurred. *s* signifies that the line was sharp.

anode and extra cathode respectively, and there is consequently a double anode fall and a double cathode fall of potential to be overcome by the E.M.F. applied from the induction coil. The result of this is that a larger potential difference is established between the terminals of the tube. The Leyden jars become charged to a higher potential, and the energy of the discharge is now much greater than before, as is shown by the difference in the sparks. This increase in the energy of the discharge is possibly the cause of the production, and certainly the cause of the agitation, of those vibrating systems which are the origin of the extra lines appearing in the spectrum when the mercury collects in the capillary of the tube.

That an increase in the energy of the discharge, due to an increase in the difference of potential between the terminals of the tube, is the cause of the

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appearance of these extra lines may be shown in another way, for, starting with both bulbs fairly warm and the discharge running easily, we can increase the potential gradient in the tube by lowering the flames and allowing the temperature, and therefore the pressure, of the mercury vapour to fall. Doing this, we find that the five-line spectrum changes into Spectrum II, without the blob of mercury forming in the capillary. The temperature at which this happens is lower than that at which Spectrum III is produced in the experiment described above. Having obtained Spectrum II in this manner, we can suddenly still further increase the potential gradient by tapping the tube so that the mercury collects in the capillary. The spectrum at once changes in a remarkable manner; the orange line 6152 comes out brilliantly, and is the *only* line in that part of the spectrum—the other orange and the red lines disappear. The visible lines are recorded in column IV of Table I. When the mercury falls out of the capillary the spectrum changes back again to Spectrum II. It is interesting to note that just as Spectrum II could be produced without the formation of the blob of mercury in the capillary, so, at still lower pressures, Spectrum IV would appear in the same way. It was seen on several occasions after turning out both the Bunsen burners under the tube and allowing it gradually to cool down. On these occasions there was a small spark gap (about 0·5 mm.) in the Leyden jar circuit, and feeble sparks passed across. If the pressure falls too low, heavy sparking occurs and many more lines appear in the spectrum.

The behaviour of the orange line 6152 is peculiar. Its appearance seems to depend upon circumstances which only slightly affect other lines usually appearing with it. For instance, when one limb only of the tube was warmed and the pressure of the vapour inside was not too low, the five-line spectrum normally changed into Spectrum III when a blob of mercury collected in the capillary, but sometimes all the lines of this spectrum would appear except 6152. On these occasions, by careful observation, the line could usually be seen very faintly, and it would suddenly flash out quite brilliantly for an instant, probably during some slight change in the electrical conditions. At the same time several of the other lines would momentarily increase in brightness, notably the yellowish-green line 5679. It might here be mentioned that I made some experiments with mercury vacuum tubes containing a little helium gas, in order to have present some lines of known wave-length for standardising the readings of the spectrometer. It is well known that the presence of helium brings out the mercury orange line very brightly, when otherwise only the five-line spectrum would appear. I found that the helium lines and the mercury line 6152 always

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appeared and disappeared together as the electrical conditions were changed. They were visible when an induction coil discharge was passed with the mercury electrodes cold, but when these were heated so as to increase the vapour pressure in the tube, the helium lines would gradually get fainter and finally disappear, and so also would the mercury orange line; at the same time the other five mercury lines (Spectrum I) would gradually increase in brightness. Similar results were obtained when the discharge from a glowing lime cathode was used to produce the luminosity, although in this case the helium spectrum was always faint, and in this case, too, the other lines of Spectrum II appeared at first, but faded away as the temperature was raised. The normal cathode fall of potential in helium gas is considerably less than that in mercury vapour, and the presence of helium would therefore probably increase the potential gradient along the rest of the tube, but it is evident that neither a decreased cathode fall nor an increase in the potential gradient along the luminous discharge can be the cause of the production of the line 6152, for in the absence of helium it does not appear in the spectrum of the glowing lime discharge, although the cathode fall is always very small and the potential gradient can readily be varied, nor would such an explanation account for the intimate connection of this particular mercury line with the brightest lines of the helium spectrum.

In regard to the lines recorded in Table I, it should be stated that those down to the bright yellows 5791, 5770, were measured as accurately as possible with the spectrometer used, which had been standardised in the manner already described. The more refrangible lines were merely identified from the measurements of Eder and Valenta, which are given in the last column.

It has already been stated that at very low pressures a spectrum was obtained containing several new red and orange lines. This spectrum in the more refrangible portions corresponds to the many lined spectrum discovered by Eder and Valenta. It was first observed on turning out both the flames used to heat the vacuum tube and allowing it to cool down, but under these circumstances the tube soon becomes so hard that the discharge through it ceases. However, by careful regulation of the size of the flames and the distance of them from the tube, the temperature can be so adjusted that the many lined spectrum is continually present. It is necessary to have the Leyden jars in the circuit, and the spectrum is brightest when loud intermittent sparks pass between the knobs of the spark gap. If the sparks are weaker and give a continuously hissing noise (as they do when the pressure is not sufficiently low) only about half the number of lines are seen. The

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many-lined spectrum can be obtained at a slightly higher pressure by arranging that some mercury should collect in one of the capillaries of the tube. Under these circumstances the spectrum is brighter than at the very low pressure, but under the latter condition the lines are all quite sharp, whereas some of them appear blurred and obscured by bands at the higher pressures. The red and the orange lines only of this spectrum are given in Table II, which for comparison also contains the lines previously observed by Hermann and by Eder and Valenta.

Table II.—The Red and Orange Lines of the Many Lined Spectrum.

Lines measured in the present research.	Intensity.	Lines measured by Hermann.	Intensity.	Lines measured by Eder and Valenta.	Intensity.
		7083	1		
(6908)		6908	4		
(6717)		6717	1		
6524	3				
6521	2				
6504	4*i*				
6421	2				
6397	3				
6386	2				
6363	4			6364	2
6347	3*i*				
6318	6*i*				
6298	1				
6292 }	6*i*				
6290 }	1*i*				
6268	1				
6242	2				
(6235)	2	6235	10		
6219	2				
6187	1				
6171	3*s*				
6152	10			6152	10
(6124)	2	6124	10		
6101	2				
6090	2				
(6074)	2	6073	10		
6046	2*s*				
6023	2*s*				
6018	2				
5963	1				
5948	1				
5936	1*s*				
5890	7	5890	2	5889	4
5881	2			5881	2
5873	7	5872	1	5872	6

i signifies that the line was intermittent; the intensity given is that of the line at its brightest.
s signifies that the line was sharp.
The lines 6292, 6290, usually alternated, first one, then the other, appearing in rapid succession.

On a few occasions lines were seen in the red beyond 6524, but I was unable to measure the position of these with any accuracy on account of

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their feeble intensity. They appeared to be the two lines 6908, 6717, each of intensity less than 1, with other rather brighter, but very indistinct lines at about 6642, 6604, and 6555. I am inclined to think that the five red and orange lines of the spectrum of the glowing lime discharge (which are placed within brackets in the table) do not properly belong to the many-line spectrum, for they were absent when the spectrum was at its best. If the conditions of the discharge slightly changed, however, the three orange lines 6235, 6124, 6074, would appear, and often when the mercury fell out of the capillary the spectrum would change to Spectrum II of Table I with these lines extraordinarily brilliant. After a few seconds—probably as the temperature fell—hissing sparks would be heard between the knobs of the spark gap and several lines of the many-lined spectrum would appear. The sparks would change to loud intermittent ones when the condensed mercury fell and stopped up the capillary, and then the complete many-lined spectrum could again be observed.

In the table a few of the lines are marked as intermittent; these, as a rule, kept flashing in at very frequent intervals, but in the case of 6318 the line was present all the time and kept flashing out more brightly. These intermittent lines were the last to appear in the many-lined spectrum as the pressure of the mercury vapour in the tube fell.

It has been mentioned that when the many-lined spectrum was obtained at the higher pressure by waiting for a blob of condensed mercury to collect in the capillary of the tube, some of the lines were blurred and obscured by bands. As examples of this: a faint band occurs between the lines 5963 and 5936, but when the many-lined spectrum is at its best this goes, and the line 5948 is seen quite plainly, while the line 5936 becomes extremely sharp. In the same way a band between the lines 6046 and 6018 at the higher pressure disappears when the pressure is reduced, leaving the line 6023 sharply defined.

The many-lined spectrum may conveniently be obtained in another way, by passing an electrodeless ring discharge through mercury vapour. This was done with the tube shown in fig. 2 in the following manner:—The tube was placed on its side and most of the mercury was collected in the bulb B. The bulb A was surrounded by a coil of 10 turns of well-insulated wire, the ends of which were each connected to the outer coating of a large Leyden jar. The inside coatings of these jars were connected to the induction coil with an electric valve in series. An adjustable spark gap was arranged between the two inside coatings, and as each spark passed across this, there was a luminous ring discharge in the bulb A, if the temperature of the tube was first adjusted so that the pressure of the mercury vapour was within certain

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limits. The author had previously found* that very bright luminosity may be produced in a gas in this way at pressures as low as 0·03 mm.—corresponding in this case to a temperature of about 60° C.

The electrodeless discharge only gives the complete many-lined spectrum when the slit of the spectroscope is directed to the outer edge of the luminous ring. Fewer lines were seen on looking nearer to the centre of the bulb, where the field is less intense, but these were always lines belonging to the many-lined spectrum; the spectra recorded in Table I were never obtained from the electrodeless discharge.

In addition to the red and orange lines recorded in Table II, 66 other lines were measured in the more refrangible parts of the many-lined spectrum. As nearly all of these were identified as lines measured by Eder and Valenta, it was thought to be unnecessary to give them here. It should be mentioned that the lines in the second column of Table II were measured by Hermann in the spectrum of the mercury arc, produced in an Arons lamp. Hermann used a special method of rendering his photographic plates sensitive to the red rays. There can be no doubt that it was the absence of such sensitiveness in the plates used by Eder and Valenta that was the cause of the lines now recorded in this region of the spectrum escaping detection in their experiments.

Summary and Conclusion.

The experiments described in this paper go to prove that mercury is capable of giving several distinct line spectra when subjected to an electric discharge in a vacuum tube. The particular spectrum appearing in any given case depends upon the energy of the discharge in relation to the mass of vapour through which it passes. The five-line spectrum is the one most easily produced, and as the energy is increased, or the pressure of the vapour is diminished, the other spectra recorded in the tables make their appearance in turn. The spectra of Table I are all perfectly definite in appearance, not only in regard to the actual lines they contain, but also as to their relative intensities when the spectrum is fairly bright; moreover, on gradually increasing the energy of the discharge, all the lines of each spectrum in turn appear at the same moment as the electrical conditions become suitable to its production. The many-lined spectrum, on the other hand, is not quite so definite, for the number of lines appearing increases as the energy of the discharge is increased, until all are present. This is well illustrated by the case of the electrodeless ring discharge, in which, as has already been mentioned, the complete many-lined spectrum is only seen in the stronger parts of the field. A similar

* Horton, 'Roy. Soc. Proc.,' A, 1910, vol. 84, p. 434.

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result can be obtained with the ordinary vacuum tube discharge in which the electrical intensity is different at different points. It is much greater in the capillary portion than in the wider parts of the tube; and, consequently, when the complete many-lined spectrum is seen in the capillary, there may be many fewer lines in the spectrum of the luminosity at other places. This is the result obtained by Huff, which is referred to at the commencement of this paper. Huff came to the conclusion that the change from the spectrum with fewest lines to that with the greatest number is quite gradual. This is so when we are dealing with the many-lined spectrum all the time—and I class the two spectra of Eder and Valenta (and also those of Stark) together, as being the same spectrum, with many more lines visible in one case than in the other—but this gradual change does not occur in the case of the spectra of Table I, all of which contain many fewer lines.

It will be noticed from the tables that the five lines of Spectrum I are common to all the spectra of mercury, though their relative intensities are not always the same. The spectrum of the glowing lime discharge consists of these plus some others, the brightest being the three lines in the orange region. Spectrum III is practically a combination of Spectra II and IV, together with a few extra lines, the brightest of which is 5366. There are seven lines of Spectra II and IV which do not appear in Spectrum III, but all are of very small intensity. The many-lined spectrum contains all the lines of the other spectra, except the five red and orange lines 6908, 6717, 6235, 6124, 6074. These, though sometimes visible, were always absent when the spectrum was at its best.

In conclusion, the author would like to emphasize the importance, from a spectroscopic point of view, of two of the methods of producing luminosity in a gas which have been employed in these experiments, namely, by using the electrodeless ring discharge, and by the discharge from a glowing lime cathode. The first of these is a very convenient way of obtaining the spectrum with most lines, corresponding to that given by a heavy discharge with capacity in the circuit. The latter method of exciting luminosity is one which should be capable of many applications in spectroscopy, on account of the ease with which the electrical conditions can be controlled.

In many respects mercury would appear to be an ideal substance to use for investigating the origin of spectra, for its vapour is monatomic and is very easily ionised; moreover, it is possible to excite luminosity in it in several ways: by the electric arc or spark, or by the vacuum tube discharge. This latter may be produced (*a*) under a high potential difference, as with an induction coil—and here the conditions may be varied by introducing capacity

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and self-induction into the circuit; (*b*) under a low potential difference by means of the discharge from a glowing lime cathode; and (*c*) by electromagnetic induction in the electrodeless ring discharge. Under these different conditions a continuous spectrum, a band spectrum, and spectra with various numbers of bright lines may be obtained. The difficulty is to correlate the observed spectra with the electrical conditions producing them.

The author gladly takes this opportunity of expressing his thanks to Prof. Sir J. J. Thomson for his interest in these experiments, which were carried out in the Cavendish Laboratory, Cambridge.

The Specific Heat of Water.

By W. R. Bousfield, M.A., K.C., and W. Eric Bousfield, B.A.

(Communicated by Prof. Sir J. Larmor, Sec. R.S.,—Received January 19;—Read February 23, 1911.)

(Abstract.)

The object of this investigation was to obtain a basis curve for the specific heat of water, for comparison with specific heat curves of aqueous solutions. Former observers using different methods have obtained widely varying curves; thus for the specific heat of water at 80° in terms of the 15° calorie, the following figures have been given, showing differences of 1 per cent.:—Barnes, 1·0014; Regnault, 1·0081; Lüdin, 1·0113.

For the value in joules of the 15° calorie the following have been found:—Joule, 4·174; Griffiths, 4·198; Barnes, 4·184.

The first part of our investigation is concerned with the determination of the mechanical equivalent of heat in terms of the mean calorie from 13° to 55°, by a method of continuous flow calorimetry. Mercury thermometers were used which could be read to 0°·005. An interval of 40° was taken, so that an error of 0°·01 would not vitiate the result by more than 1 in 4000. Through a Dewar vessel containing about 3 litres of water, in which was an electric heater, there was passed a current of water, entering at about 13° and passing out at about 55°. The vessel was immersed in a bath kept at the same temperature as the contents of the vessel. The top of the vessel was closed by a platinum box kept 10° higher.

The electric heater, and the resistance used in series with it for determining the current by help of a battery of standard cells, were of novel type. Each consisted of a spiral glass tube of small bore into the ends of which were sealed platinum electrodes. The tube is connected with a thermometer tube so that

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the spiral forms a thermometer bulb. By calibrating the resistance against the reading of this thermometer tube, the resistance is accurately known, even when a current is passing. This type of resistance enabled us to surmount a difficulty apparently never considered by previous investigators. We have found that when a heavy current passes through an ordinary standard resistance, the resistance of the standard depends not only on temperature but also upon strength of current. The passage of the current appears to induce a state of strain which temporarily alters the resistance by an amount which may be as much as several units in 10,000. The residual effect on the resistance when the current ceases has long ago been observed, particularly as a hysteresis effect with manganin resistances. The change which persists whilst the current is passing may be conveniently called the "thermoid" effect. We believe a liquid mercury resistance is free from any such effect.

The continuous-flow experiments gave for distilled water $J_{13}^{55} = 4{\cdot}182$. To get the curve for J from 0° to 80°, a weighed quantity of water was heated from 0° to 80° by stages which gave J_0^{13}, J_{13}^{27}, J_{27}^{55}, J_{55}^{80}, the mean specific heats over the intervals. For this purpose the capacity of the calorimeter was obtained from the value of J_{13}^{55}, previously determined, and a separate research on the specific heat of glass was carried out in order to obtain the variation of capacity with temperature. From these mean values of J for the intervals an equation for the value J_0^{θ} was obtained, and then the value of J from point to point from the equation

$$J = \frac{d}{d\theta}(\theta J_0^{\theta}).$$

We thus obtain $J = 4{\cdot}2085 - 0{\cdot}003022\theta + 0{\cdot}00007833\theta^2 - 0{\cdot}0000004490\theta^3$, which gives for the value of the 15° calorie 4·179. The resulting curve corresponds closely with that obtained by Lüdin by the method of mixtures, and differs considerably from that obtained by Barnes* by continuous flow with platinum thermometry. The values of J obtained by us are as follows:—

θ.	J.	θ.	J.	θ.	J.
0	4·209	30	4·175	60	4·203
5	4·195	35	4·178	65	4·208
10	4·186	40	4·182	70	4·213
15	4·179	45	4·187	75	4·216
20	4·176	50	4·192	80	4·217
25	4·174	55	4·198		

* Barnes' latest values corrected for the value of the Clark cell used by him are given in 'Roy. Soc. Proc.,' 1909, A, vol. 82, p. 390.

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The minimum value for the specific heat of water has been placed at various temperatures by different observers. Regnault found no minimum value; other observers have placed it as follows:—

Bartoli and Stracciati ...	20°	Rowland.....	30°
Lüdin	25°	Barnes	38°

Our value for the minimum agrees with that of Lüdin.

Memoir on the Theory of the Partitions of Numbers. Part V.—*Partitions in Two-dimensional Space.*

By Major P. A. MacMahon, D.Sc., F.R.S.

(Received December 31, 1910,—Read January 26, 1911.)

(Abstract.)

This paper is principally concerned with the enumerations of the partitions of numbers in two-dimensional space. Such partitions are such that the parts are placed at the points or nodes of a lattice, rectangular in shape, and

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having given numbers of nodes in the sides, and the parts of the numbers partitioned are placed at the nodes in such wise that descending order of magnitude in each row of parts is from left to right and in each column of parts from top to bottom.

If the nodes in the sides be m, n, respectively, and the part magnitude be restricted so as to be not greater than l, the generating function which gives by the coefficients of x^w in the ascending expansion the number of such partitions of the number w has been long conjectured by the author to have the expression

$$\frac{\begin{matrix}(l+1)(l+2)\dots(l+m)\\ (l+2)\dots(l+m+1)\\ \ddots\qquad\qquad\ddots\\ (l+n)\dots(l+m+n-1)\end{matrix}}{\begin{matrix}(1)(2)\dots(m)\\ (2)\dots(m+1)\\ \ddots\qquad\ddots\\ (n)\dots(m+n-1)\end{matrix}}$$

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where (s) denotes $1-x^s$; but previous attempts to establish this had, except in certain particular cases, resulted in failure.

The present communication shows that the generating function may be written

$$\sum_{s=0}^{s=(m-1)(n-1)} \frac{(l-s+1)\dots(l-s+mn)\,\mathrm{L}_s}{(1)\dots(mn)},$$

where the functions L_s are readily derivable from any given lattice, and the only question thereafter is the examination of these functions and the simplification of the expression for the generating function.

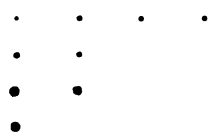
Considerable progress is made with these matters, and it is shown that if the conjectured form be true when l does not exceed mn, it must be true in general.

Further, that if the simplified form be assumed to be composed entirely of powers of factors

$$(s),\ (l+s),$$

where s is free from l, the form must be that which has been conjectured.

The method is equally valid for partitions at the points of an incomplete lattice in which the rows do not contain the same numbers of nodes, *e.g.*,



and a further study of these is necessary before the main result can be considered as established with complete rigour. This will form the subject of another communication to the Society.

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An Optical Method of Measuring Vapour Pressures: Vapour Pressure and Apparent Superheating of Solid Bromine.

By CLIVE CUTHBERTSON, Fellow of University College, London, and MAUDE CUTHBERTSON.

(Communicated by Prof. F. T. Trouton, F.R.S. Received April 20,— Read May 25, 1911.)

In the course of an investigation of the refractivity of gaseous bromine conducted with a Jamin refractometer it was observed that, as the temperature changed, very slight variations of the density of the vapour could be quickly and accurately recorded. This fact suggested that an optical method would be useful for measuring vapour pressures or densities at low pressures, especially in the case of substances which attack mercury. The following observations on the vapour of bromine serve as an illustration of the possibilities of the method, and have brought to light an interesting phenomenon, which is described below.

A thin glass bulb, containing 1 or 2 c.c. of Kahlbaum's pure bromine, was sealed to a tube communicating both with the pump and the refractometer tube. The temperature of the bromine was reduced to $-80°$ C., at which its vapour pressure is negligible, and the bulb was completely evacuated, so as to remove all traces of hydrobromic acid which might have formed by the action of the bromine on the tap-grease since the previous experiment. The refractometer tube was separately evacuated, and the two were put in connection by opening a tap. The cooling bath was then slowly brought up to atmospheric temperature by stages, while an observer counted the interference bands which crossed the field of view of the refractometer.

During each reading the temperature of the bulb was kept constant by stirring the bath. As the melting-point was approached numerous readings were taken, the rise of $1°$ from $-8°$ to $-7°$ sometimes occupying 20 minutes. A complete series of readings between $-80°$ and $0°$ occupied about an hour. At the moment of each reading the temperature of the refractometer tube was also read. The light used was approximately monochromatic, and had the wave-length of the red Cd line, 6438.

In this experiment what is actually observed is the temperature of the liquid bromine and the corresponding refractivity of the vapour in the refractometer tube, which is at the same pressure as the vapour in contact with the liquid, though at a different temperature. The refractivity of bromine vapour for a known density had previously been determined by us,

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and if we assume that the refractivity is proportional to the density, as Mascart's work justifies us in doing, then the density of the vapour in the refractometer tube is known for various temperatures. It may further be assumed that, at the low pressures at which measurements were taken, the pressure of the vapour in the tube is proportional to its density. Hence, if we know one pressure and temperature absolutely, the whole curve of temperatures and pressures can be calculated from these observations.

Ramsay and Young* found for bromine at its melting point a pressure of 44·5 mm.

Assuming this value, the table below shows the vapour pressures derived from a typical set of readings which are well supported by other series.

Vapour Pressures of Solid Bromine.

Temp. (C.)	Pressures (mm.)			Temp. (C.)	Pressures (mm.)		
	Observed.	Calculated.	Difference.		Observed.	Calculated.	Difference.
−80°	0·13	0·13	0	−15°·7	22·9	22·34	−0·56
−64°·75	0·52	0·48	−0·09	−15°·1	24·35	23·44	−0·91
−63°	0·66	0·5	−0·16	−12°·7	28·8	28·41	−0·39
−59°·9	0·79	0·65	−0·14	−12°·5	29·9	28·87	−1·03
−53°·3	1·05	1·1	+0·05	−10°	36·15	35·27	−0·88
−46°·9	1·83	1·83	0	− 9°·6	37·1	36·42	−0·68
−41°·3	2·89	2·87	−0·02	− 7°·7	42·25	42·41	+0·16
−28°·8	7·74	7·82	+0·08	− 7°·5	42·9	43·1	+0·2
−28°·3	8·14	8·14	—	− 7°·2	43·9	44·14	+0·24
−22°·6	13·0	12·82	−0·08	− 7°·1	44·5	44·5	—
−19°·4	16·7	16·61	−0·09				

If the values of p are plotted against the absolute temperatures the points fall on an exponential curve

$$p = ab^{\theta},$$

where $a = 2{\cdot}485 \times 10^{-8}$ and $b = 1{\cdot}0834$.

The values of p, calculated from this equation, are shown in the third column. The constants were derived from the values $p = 44{\cdot}5$ and 8·14. At −12°·74 C., Ramsay and Young found $p = 28{\cdot}1$ mm. The number calculated from the formula above is 28·3. At −17°·12 they found $p = 18{\cdot}9$ against 19·9 calculated. Thus the two sets of observations agree well.

Numerous observations were taken at and about the melting point, both with ascending and descending temperatures, and on several occasions, though not on all, an interesting fact was observed. With steadily rising temperature of the bath the vapour pressure at the melting point increased

* 'Chem. Soc. Journ.,' vol. 49, p. 457.

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above 44·5 mm. by 1 or 1½ mm., and then, in the course of one or two minutes, fell back again. After remaining almost constant for a few seconds it then began to jump several times and fall back again, and at last it mounted steadily and rapidly. At each jump, which lasted one or two seconds, the pressure rose by 1 or 2 mm.

A corresponding result was observed with falling temperature of the bath, the vapour pressure suddenly rising and then decreasing, but without jumping.

These phenomena may possibly be due to differences of temperature between neighbouring portions of the solid in the bulb, vapour being formed at one place and condensed in another. But they are more probably explicable as the changes which might be expected to occur during the superheating of the solid and supercooling of the liquid. The superheating of a solid is stated by Chwolson to have been observed by Barus in the case of naphthalin; and Duhem gives instances of a similar phenomenon in connection with the passage of a solid from one crystalline form to another.

Whatever be the cause, the optical method seems to promise a valuable means of investigating the rapid and delicate changes of vapour pressure which must occur at the freezing point. Jamin's form of interferometer is, of course, not indispensable. The simple design described by Lord Rayleigh, and used by Ramsay and Travers for the inert gases, would prove equally efficient.

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The Influence of Planets on the Formation of Sun-spots.

By Arthur Schuster, F.R.S.

(Received in abstract and read March 23,—Complete MS. received May 3, 1911.)

1. This investigation deals with the correlation between the position of sun-spots at their first appearance and the heliocentric longitude of the principal planets. The available data reach back as far as 1874 inclusive, and are to be found in the publications of the Royal Observatory, Greenwich.

If we neglect the angle between the sun's equator and the ecliptic, and add the heliocentric longitude of the earth to the longitude of a spot referred to the central meridian, we obtain the heliocentric longitude of the sun-spot measured from the first point of Aries; deducting now the heliocentric longitude of a planet, we obtain the longitude of the spot referred to the central meridian as seen from the planet. Excluding spots near the eastern limb, many of which have been formed on the invisible hemisphere and are brought into view by the sun's rotation, the first photograph on which a spot appears gives the position of its origin within about 13° of longitude, provided there are no gaps in the daily records. For the reason given, no account has been taken of any spot which is first seen within 30° longitude from the eastern limb. Measured on the projected disc, the excluded portion covers at the equator a width of 2 minutes of arc or about the eighth part of the solar radius. The total number of spots dealt with is 4271.

2. Any planetary influence that may exist probably depends on the distance of the planet from the sun, and possibly on its mass and size, and in whatever way we combine these factors they point to Jupiter, Venus, and Mercury as most likely to be effective. I shall therefore deal primarily with these planets.

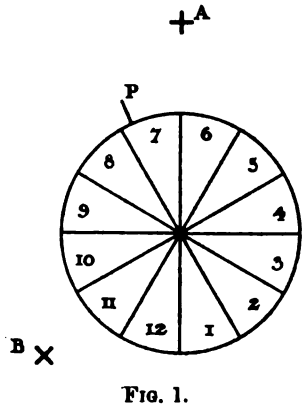

Fig. 1.

The position of the spot at its first appearance as seen from the planet having been obtained in the manner described, the solar surface was divided by circles of longitude into 12 equal compartments, starting with that meridian circle which is directly opposed to the central meridian as seen from the planet. Fig. 1 represents a section of the sun by the ecliptic and its division into compartments when a planet A is under discussion. The compartments are supposed to revolve with the planet, and, except at conjunction, they are

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different for each planet, so that the spot at P formed in division 7, when the planet A is considered, would be entered as forming in division 3 in relation to a planet situated at B if its angular distance from B measured anti-clockwise is between 240° and 270°.

The whole available period of 36 years was divided into three groups. In the case of Jupiter and Mercury, each group included 12 years, but in the case of Venus the discussion was conducted on the basis of synodic revolutions instead of years, and the first group contains the spots which were observed during the eight synodic revolutions beginning with September, 1875, while the second and third groups each include the spots seen during the seven succeeding synodic revolutions.

3. Table I gives for each of the three planets and for each of the three groups the numbers of the spots first seen in the compartment indicated at the head of the columns. The last column gives the total number of spots in the group. Fig. 2 shows in diagrammatic form the number of spots which first appeared in each compartment during the whole period of 36 years. The curves are given separately for each planet and a fourth curve is added showing the average result for the three planets combined. In fig. 2 the curves are drawn taking account of the last group of years only. In the tables the heavier lines indicate divisions of the sun according to the quadrants, the centre line representing the central meridian. In the figures, short lines indicate the compartments, while the vertical lines passing through the figures indicate divisions according to quadrants, the central line representing the central meridian. On the vertical scale the distance between two horizontal lines drawn at the margin is 20 spots in fig. 2, and 10 spots in figs. 3, 4, and 5.

The remarkable difference, first pointed out by Mrs. Maunder, in the number of spots which make their first appearance respectively in the eastern and western half of the solar disc, made it advisable to separate the spots according to their position on the solar disc.

In Table II the whole period of 36 years is combined, but the spots are divided into three groups according to their position at first appearance. Group A includes all spots which are first seen between 60° and 30° east of the central meridian, while B refers to longitudes east between 30° of the central meridian, and C to all spots seen west of the central meridian. Fig. 4 gives in diagrammatic form the frequencies of first appearance of those spots west of the central meridian, while fig. 5 refers to those which first appear east of the central meridian, and which during their rotation round the sun's axis have not yet therefore passed it.

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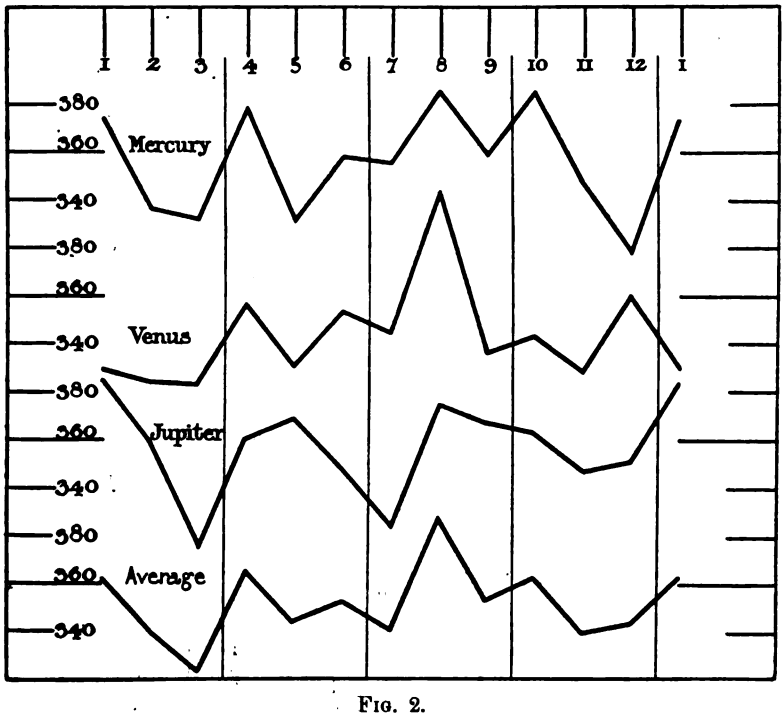

FIG. 2.

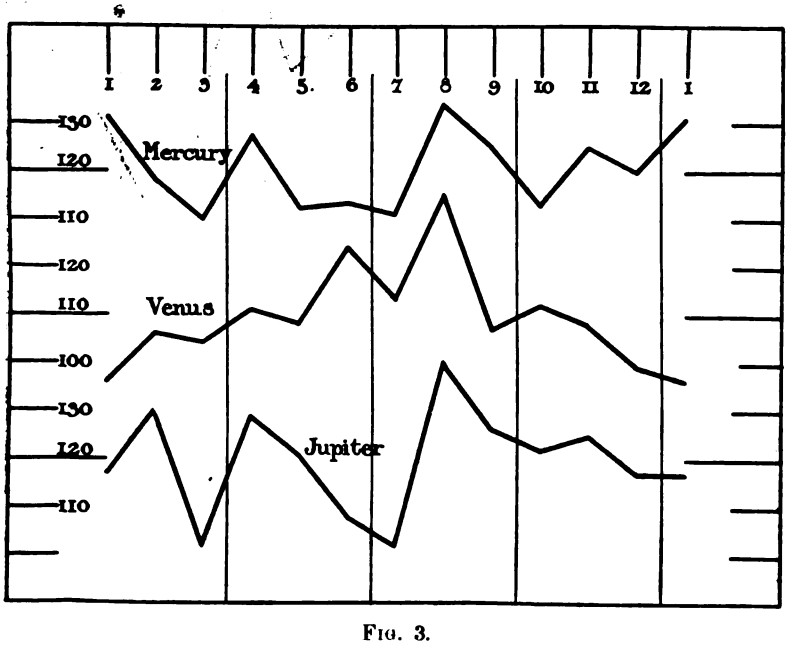

FIG. 3.

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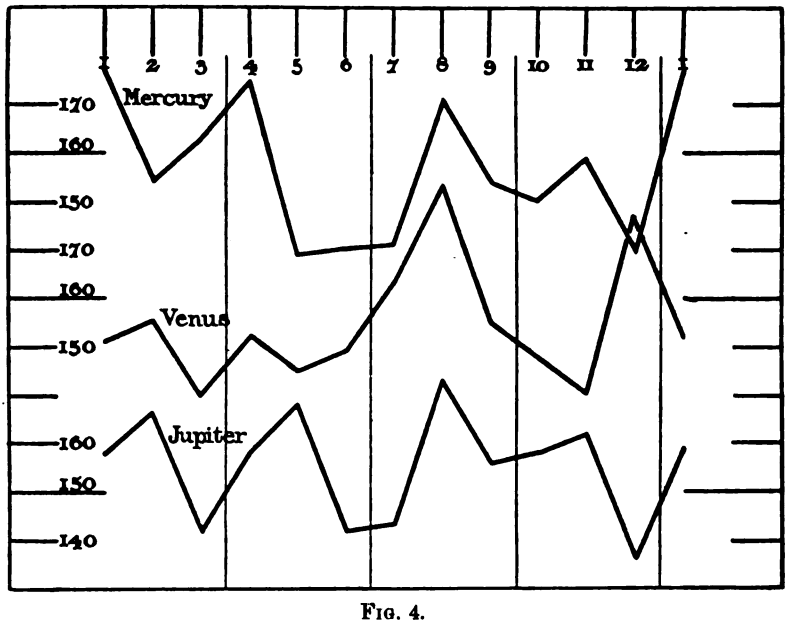

FIG. 4.

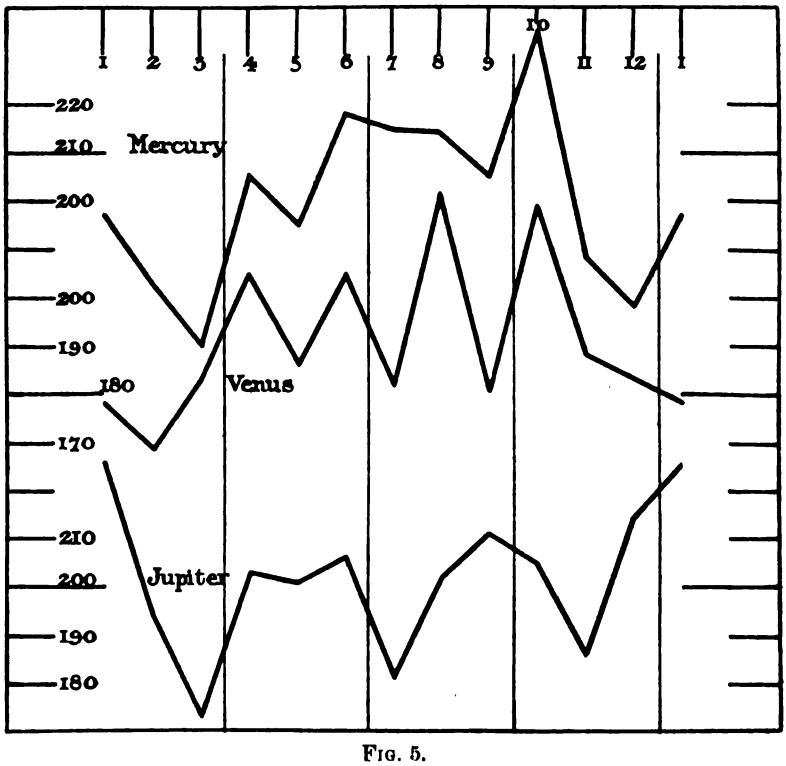

FIG. 5.

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Table I.

Planet.	Group.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	Sum.
Mercury	I.....	99	97	88	104	84	89	92	96	85	106	84	71	1095
	II.....	144	122	135	148	138	156	153	155	149	166	138	127	1731
	III.....	131	118	110	127	112	113	111	134	125	113	125	120	1439
$\Delta = 18{\cdot}0$	Sum.....	374	337	333	379	334	358	356	385	359	385	347	318	4265
Venus	I.....	98	94	88	103	95	91	97	111	96	99	81	111	1164
	II.....	135	124	131	143	128	139	135	158	133	132	139	150	1647
	III.....	96	106	104	111	108	124	113	135	107	112	108	99	1323
$\Delta = 16{\cdot}2$	Sum.....	329	324	323	357	331	354	345	404	336	343	328	360	4134
Jupiter	I.....	90	86	86	78	89	93	87	96	104	97	93	96	1095
	II.....	178	144	127	154	159	147	135	139	137	144	129	138	1731
	III.....	117	130	102	129	121	108	102	140	126	122	125	117	1439
$\Delta = 15{\cdot}3$	Sum.....	385	360	315	361	369	348	324	375	367	363	347	351	4265
Average for three planets	...	362	340	323	365	344	353	341	388	354	363	340	343	4221

Table II.

Planet.	Longitude.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	Sum.
Mercury	A, $-60°, -30°$	111	88	83	112	98	112	103	117	105	127	104	78	1238
	B, $0°$ to $-30°$	86	95	87	93	97	106	112	97	100	108	84	100	1165
	C, $0°$ to $+90°$	177	154	163	174	139	140	141	171	154	150	159	140	1862
Venus	A, $-60°, -30°$	79	83	97	104	92	99	109	109	85	108	91	102	1158
	B, $0°$ to $-30°$	99	86	86	101	94	106	73	112	96	110	97	81	1141
	C, $0°$ to $+90°$	151	155	140	152	145	149	163	183	155	125	140	177	1835
Jupiter	A, $-60°, -30°$	112	102	109	111	82	105	95	101	112	102	98	109	1238
	B, $0°$ to $-30°$	114	92	64	92	119	101	86	101	99	103	88	106	1165
	C, $0°$ to $+90°$	159	166	142	158	168	142	143	173	156	158	161	136	1862

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For the purpose of comparison it appeared to be desirable to test also some planet from which no effect was to be expected. Mars and Saturn were chosen for the purpose, and the results are given in Table III. Saturn was treated, however, in a somewhat simplified manner, its heliocentric position

Table III.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	Δ.
Mars.....	337	330	360	352	391	361	374	364	361	326	357	352	13·3
Saturn ...	323	363	330	359	381	396	357	371	372	338	330	341	18·9
Aries.....	375	339	394	357	332	373	351	362	367	307	340	364	17·6

being considered constant during each year, and suddenly altered at the end of it. It may be mentioned incidentally that this investigation originated in the desire to find a possible regularity in the birthplace of spots looked at from a fixed point in space. While laying the discussion of this part of the subject aside for the present, I include in the table the statistics resulting from considering an imaginary planet fixed in space at the first point in Aries; the name of this constellation is attached to the number referring to this imaginary planet.

4. I may now briefly discuss the conclusions to be drawn from the tables and figures. I must insist at once, that the variability of the numbers given in the different compartments is not by itself sufficient to indicate any planetary effect. Even though the formation of sun-spots were quite independent of the position of the planets, we should still have differences in the compartments, and the laws of probability lead us to expect that these differences would not be very much smaller than those actually exhibited in the tables. The argument for the real existence of a planetary effect rests entirely on the similarity in the apparent effect of the three important planets. An inspection of fig. 2 shows that in the formation of spots, the compartment 3 has a minimum in all three cases. An observer stationed in that compartment on the sun would have the planet just below his eastern horizon and about to rise. If the complete rotation of the sun be divided into 24 hours, the imaginary observer would find an increased effect within the first two hours after the planet has arisen. This is followed by a diminution in the activity, finally rising again to a decided maximum about three hours after the planetary noon (compartment 8). Without looking into details, in which we must expect irregularities, I think that agreement in the general features of the curves for Mercury and

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Venus (fig. 2) is remarkable. The only discrepancy occurs in compartment 12, or probably, rather, in compartment 1, which in the case of Venus is unduly depressed. Though Jupiter is not quite as concordant, the minimum in compartment 3 is well marked, and the maximum in 8 unmistakable. Fig. 3 shows that the principal features of the curves are found in the observations made during the last 12 years only. Figs. 4 and 5 are somewhat puzzling; they seem to show that the regularities exhibited by the spots as a whole are mainly due to those spots, which make their first appearance on the western half of the sun's disc. Though some similarity may be traced in the curves of Venus and Mercury in the spots first appearing in the eastern portion, the type of the regularity seems to be changed except for the minimum at or near 3, which persists. This matter will be further referred to in § 6, but one peculiarity may here be noted: a maximum in compartment 10, which for the combined spots (fig. 1) is pronounced only in the case of Mercury (accidentally or otherwise), is here found also with Venus, and to be due to those spots which first appear east of the central meridian. There seems, indeed, to be a tendency of this maximum to replace the one in compartment 8.

The observations are not sufficiently extended to give any information as to the differences in magnitude or kind which may exist between the effects of different planets. Mercury and Jupiter seem to indicate an increased activity on that side of the sun which is turned away from a planet, while Venus does *not* show this increase. Further observations are needed before we can decide whether the difference is real.

5. The question naturally presents itself whether two planets, acting in conjunction, have an influence which is greater than the one to be expected by mere superposition. I have therefore collected all cases in which the compartment of first appearance had the same numerical value for any two of the planets Mercury, Venus, and Jupiter, or for the three combined. The result is given in Table IV, and is not very conclusive.

Table IV.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	Sum.
Mercury and Venus	33	22	21	32	21	20	32	35	27	34	34	23	334
Mercury and Jupiter.....	16	20	16	30	19	26	25	23	21	25	20	23	264
Venus and Jupiter.....	23	25	22	26	34	27	26	30	34	40	25	29	341
Sum	72	67	59	88	74	73	83	88	82	99	79	75	939

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But though the number of spots dealt with is much reduced, the distribution in the different compartments is very similar. The minimum still appears decidedly in compartment 3 and the maximum remains in compartment 8 for the combination Mercury-Venus; for the summed effect of the three planets the maximum is shifted to compartment 10. The much greater number of spots appearing at conjunction when Venus is one of the planets concerned is probably significant. The distribution into compartments of twenty-five spots formed at the simultaneous conjunction of the three planets is given in Table V.

Table V.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	Sum.
Mercury, Venus, and Jupiter	0	1	4	7	1	3	1	1	0	3	2	2	25

The numbers are too few to allow any importance to be attached to the figures, because differences in the exposed hemisphere of the sun, according to the position of the earth at the time of conjunction, are insufficiently eliminated.

6. Is there any significance in these results, and may we be reasonably certain that the regularities of the past records will be repeated in the future? An application of the theory of probabilities to natural phenomena always presents the difficulty that it must compare what actually happens with what would happen on the supposition of a purely accidental incidence of events. But nothing is accidental in nature; and probably no two events are absolutely disconnected. We are forced to reason, as if the absence of any correlation between two sets of events distributes one set *relatively to the other* as if its occurrence were regulated by chance only. On this supposition we may calculate the probability that our results establish a real correlation between planets and sun-spots. Imagine the sun to be divided into 12 compartments by equidistant meridian circles; the probability (p) that any spot is first observed in any one definite compartment is 1/12, and the probability that out of N spots n shall appear in that compartment is, writing $q = 1-p$ and $m = N-n$,

$$\frac{N}{n!\,m!}p^n q^m.$$

The average value of n is pN.

If the number N be large, Stirling's theorem gives for the probability that

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the number in any compartment lies between $p\mathrm{N}-r$ and $p\mathrm{N}+r$ the expression*

$$\frac{2}{\sqrt{\pi}}\left[\int_0^w e^{-u^2}du+\frac{w}{2r}e^{-w^2}\right], \quad \text{where} \quad w=r/(2\mathrm{N}pq)^{\frac{1}{2}}.$$

In the case to be considered, the last term is small compared with the first, and its effect would be to increase the probability of a real correlation; it may therefore be neglected. Introducing the numerical factor and assuming provisionally that the probability of the number of spots being greater than $p\mathrm{N}+r$ is the same as that of its being smaller than $p\mathrm{N}-r$, I find the probability that the actually observed excesses in the compartment 8 are due to chance only, is 0·05, 0·00041, 0·138 for the planets Mercury, Venus, and Jupiter respectively. If we take each planet separately, we have to consider that there are 12 compartments, and in order to obtain the probability of a given excess occurring in some one compartment, we should have to multiply the above figures by 12. It is seen that only in the case of Venus do the numbers help to establish a real connection. But when we come to combine the results, and calculate the probability that the excesses should all occur in the same compartment, the verdict seems decisive. This probability, obtained by taking 12 times the product of the three figures, is $3{\cdot}4\times10^{-5}$. I find, similarly, for the probability of the deficiency in compartment 3, the value $1{\cdot}71\times10^{-3}$, and the probability that both effects should appear together is only $5{\cdot}8\times10^{-8}$, or 1 in 17 million.

The results of the above calculation might be seriously altered, if a number of groups of spots frequently occur simultaneously along the same meridian. It is found, indeed, that frequently a spot in the northern latitude is accompanied by a spot in the southern latitude in nearly the same longitude. Such a connection may be quite disconnected from any planetary action, but would tend to make the deviation from the mean in different compartments greater than what is expected from the theory of probability. To test to what extent this is the case, I have computed the mean deviation of the number of spots observed in each compartment from its average. The figures are given in Tables I and III, under the designation Δ. The mean value of Δ for the planets Mercury, Venus, and Jupiter is 17, and this is very little larger than the number found for the mean deviation, when the spots are examined with reference to Mars, Saturn, or a point fixed in space. The mean deviation, calculated on the supposition of an accidental distribution, is 14·4. If we treat the higher

* Todhunter, 'History of Probability,' p. 551.

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value actually found as due to the occurrence of spots in groups, and correct the previous calculation accordingly, the probability that we are being misled by an accidental coincidence becomes somewhat greater, and becomes about 2·5 parts in a million. This means that if there were 400,000 worlds like ours there would on an average be one, and only one, in which the distribution of spots would accidentally indicate a planetary effect such as the one described. We cannot go further than this for the present.

7. In a paper already alluded to, Mrs. Maunder* gave an exhaustive and important discussion of an apparent effect of the earth on the formation and growth of sun-spots. In the light of the present investigation we must conclude that, unless the earth acts very much more strongly than the other planets, the effect found by Mrs. Maunder is not a true planetary effect, but depends on the point of view from which a spot is looked at from the earth. I am here only concerned with the first formation, or, as Mrs. Maunder appropriately calls it, the birthplace of sun-spots, and Table VI shows how marked and regular is the preponderance of the number of spots born in the eastern half of the solar disc. The numbers are given in percentages of the total number observed during the three successive periods of 12 years, but the figures in the first column have little significance, because they include all spots born on the invisible hemisphere and brought into view by the rotation of the sun.

Table VI.

Period.	4.	5.	6.	7.	8.	9.	Number of spots.
1874—1885.....	41	18	15	13	10	3	1869
1885—1896.....	40	17	16	14	9	2	2909
1897—1909.....	38	18	17	14	10	3	2341
Average.....	40·0	17·8	16·0	13·7	9·8	2·7	7119

At first sight it would seem that a preponderance of one side of the sun over the other must be due to some want of symmetry in the conditions of visibility; but this is not the case. On the contrary, the preponderance of the eastern half mainly points to an increased facility of detecting a sun-spot when it is near the centre of the solar disc. It is possible to imagine a symmetrical law of visibility which would give a uniform distribution of new spots on one side of the disc and a total absence on the other.

* 'Monthly Notices R.A.S.,' 1907, vol. 67, p. 451.

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Although not altogether germane to the main purpose of this paper, a discussion of the effects of different conditions of visibility, which is not quite obvious and has never been taken into consideration, may be useful to others. A sun-spot, before it appears as such, probably exists in some preliminary stage in which it shows itself on the spectro-heliograms, but not on ordinary photographs of the sun. Imagine a spot in its invisible stage to grow at an average rate k per unit time, so that its area becomes kt at time t, and assume that it must reach a certain size s before it becomes visible. (Possibly s includes other conditions besides size.) A spot, according to this view, appears to us first, when it has been in existence during a time s/k. If it shows itself first in longitude λ, but has really been formed in longitude λ_1, the difference $\lambda - \lambda_1$ is equal to $\omega s/k$, where ω is the angular velocity at the sun's surface.

If the visibility of a spot depends on our point of view, s will be a function of the longitude of the spot where it first appears to us, and we may therefore write

$$\lambda_1 = \lambda - f(\lambda), \qquad d\lambda_1 = d\lambda\,[1 - f'(\lambda)].$$

If N_1 represents the number of spots generated in unit time in unit range of longitude, and $Nd\lambda$ the number of those which are first observed in the range $d\lambda$, we have

$$Nd\lambda = N_1 d\lambda_1 = N_1 d\lambda\,[1 - f'(\lambda)],$$

and hence

$$N = N_1\,[1 - f'(\lambda)].$$

We shall assume N_1 to be constant, and $f(\lambda)$ to have the same value for equal positive and negative longitudes. It follows that $f'(\lambda)$ will be numerically equal and have opposite signs for corresponding points in the two halves of the solar disc. For the same distance from the centre we have therefore

$$N_+ = N_1\,[1 - f'(\lambda)],$$
$$N_- = N_1\,(1 + f'(\lambda)],$$
$$N_- - N_+ = 2N_1.$$

If the centre of the disc favours the visibility, $f(\lambda)$ will be smallest when $\lambda = 0$, and $f'(\lambda)$ will be positive on the positive side, hence there will be an excess of spots which first appear to form on the negative side, which is the eastern half of the sun's disc. This excess, therefore, only proves an increased condition of visibility near the centre, but, in itself, no want of symmetry. If, as an example, we assume $f(\lambda)$ to be equal to $a + \lambda$ for the positive values of λ, and $a - \lambda$ for the negative values of λ, it would follow that the formation of spots takes place at a uniform rate of

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2N in the eastern half of the disc, but that no spot at all would be seen to form in the western half. The condition which must be satisfied, if the law of visibility is symmetrical with respect to the sun's centre, is $N_+ + N_- = 2N$. The sum in the birth rate of spots for equal positive and negative longitudes must therefore be constant in this case. Only in so far as the actual numbers do not show this constancy, but some excess for the smaller longitudes, is there any evidence for a want of symmetry in the conditions of visibility on the sun, or possibly for a change in N_1, which has been assumed to be constant.

This investigation was begun under the impression that the breaking out of spots afforded a convenient and simple test of planetary activity. The result has shown that, though convenient, it is beset by difficulties of interpretation which counterbalance the advantages of simplicity. The nature of the effect must therefore be left to future discussion.

8. Attempts to connect planets with solar activity have been made previously, and insufficient attention, perhaps, has been paid to a remarkable investigation by Warren de la Rue, Balfour Stewart, and Benjamin Loewy.* This may be due to the fact, which it would be wrong now to conceal, that Mr. Loewy, to whom, in a later series of investigations, and probably in this, the numerical work was entrusted, subsequently admitted that he had not dealt candidly with the figures. At what period he began not to do so, and whether the investigation here referred to is one of those affected, is not certain, but from my personal recollection of the history of these transactions I am inclined to believe that it is free from intentional errors. With all due reserve, we may therefore recall the important results of the investigation, which seem to have lapsed altogether into oblivion. Taking the long-lived groups of spots and treating their areas, the authors find, as Mrs. Maunder did subsequently, that the areas of the spots increase on the average as they cross the solar disc until they cross the central meridian, when they begin to decrease. But they also find, in direct opposition to Mrs. Maunder, that for equal longitudes east and west the areas are greater on the western side. The cause of this discrepancy must be left to be decided by further investigation. It is conceivably due to a systematic difference in the areas as measured from photographs or directly by eye estimate, as was done in the earlier records, or there may be some long-period change in the effect. After applying what is called an "earth correction," the authors find a very marked planetary effect, the areas being diminished at those parts of the sun which are turned towards the planet and increased at those parts which are turned away from the planet. Mercury and Venus give identical results, but none was found in the case of Jupiter. Though the

* 'Roy. Soc. Proc.,' 1872, p. 210.

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numerical work is considerable, it is highly desirable that the correctness of these results should be tested with the better material which is now at our disposal.

9. A few words may be said on the *a priori* difficulties which may be felt in accepting a direct influence of a planet on solar phenomena. The tidal effect of planets on the sun's outer shell, which has been suggested by several writers, is generally believed to be too small to be effective, but gravitational effects may be much increased if there is a layer surrounding the sun in which gravitation is to some extent counterbalanced by radiation pressure. Arrhenius, in the theories he advocates, assumes such a cloudy layer, which is kept in suspension by radiation. It is easy to calculate the residual gravitation which must remain, so that the particles may not part company with the sun, in which case they must behave like satellites circulating round the sun in his time of revolution. If r be the radius of the sun ($6{\cdot}97 \times 10^{10}$ cm.) and v the velocity which a point of the sun's equator possesses in virtue of the sun's rotation round his axis (2·03 kilom. per second), the acceleration of a particle revolving with the sun, is $v^2/r = 0{\cdot}59$. By a numerical coincidence this is also the mean acceleration of the earth in its orbit round the sun.

It follows that the residual gravitational action of the sun on its suspended clouds is to the gravitational force of the earth on these clouds, as the mass of the sun is to the mass of the earth, or 330,000 times as great. That the earth's gravitational attraction, small though it may appear to be at first sight, may yet be effective in its action, is shown by comparing it with the action of the moon on a body placed on the surface of the earth, which only amounts to the 288,000th part of the weight of the body. But when we compare the effect of the earth on the sun with that of the moon on the tide, the advantage is considerably in favour of the former, because it is not, like the tidal action, differential in its nature, having the same direction on both sides of the sun.

We are not, however, dependent on radiation pressure for a plausible explanation of a planetary action on the outer shell of the solar globe, which may be purely electrostatic. The expulsion of negative electrons from hot bodies must leave the solar clouds positively electrified. On the other hand, negative particles ejected from the sun must to some extent accumulate in the outer layer of planetary atmospheres. An estimate of the maximum electrostatic effect of the planets on the solar atmosphere is easily made, because the electrification of the planetary atmosphere cannot exceed a certain value without dissipation into space. If σ be the charge per unit surface of the atmosphere, the outward force on each electron carrying

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a quantity of electricity e will be $4\pi\sigma ec^2$, where c is the velocity of light. This cannot be greater than the weight mg of this particle, where m denotes the mass of the ion to which the charge is attached.

The whole charge (E) of a planet having a radius a is $4\pi\sigma a^2$, so that this maximum charge is determined by $Ec^2 = mga^2$. The electrostatic action of E on a charge e' at the surface of the sun, is $Ee'c^2/d^2$, if d be the distance between the two bodies and the gravitational attraction of the planet on a particle of mass m' is $m'ga^2/d^2$. We therefore reach the conclusion, that if the particles of the solar clouds have the same ratio e'/m' as charged particles in a planetary atmosphere, the electrostatic effect of the planet is equal to its gravitational effect. It need hardly be pointed out that the charge of the outer layer of its atmosphere produces no effect at the surface of a planet unless the uniformity of its distribution is temporarily disturbed. The electrification may therefore be responsible for some variation, periodic or otherwise, but not for any average effects taken over long periods of time.

The action of planets on particles ejected from the sun or returning to it may affect in other ways a delicately adjusted balance such as that which seems both electrically and gravitationally to regulate the phenomena at the solar surface, but enough has been said to show that a plausible explanation of a planetary action on sun-spots may be found without going beyond well-established processes.

Table VII, which explains itself, may assist in forming an estimate of the relative importance of different planets in their action on the sun. If the

Table VII.

Planets.	a.	m.	km/a^2.	$k'm/a^3$.	s.
Mercury	0·387	$2·0 \times 10^{-7}$	0·43	1·10	6·6
Venus	0·723	$2·5 \times 10^{-6}$	1·53	2·11	16·9
Earth	1·0	$3·1 \times 10^{-6}$	1·0	1·0	17·6
Mars	1·52	$3·2 \times 10^{-7}$	0·04	0·03	9·4
Jupiter	5·20	$9·52 \times 10^{-4}$	11·27	2·17	37·0
Saturn	9·54	$2·86 \times 10^{-4}$	1·00	0·11	18·0
Uranus	19·2	$4·42 \times 10^{-5}$	0·38	0·02	3·5

a = relative distance from sun.
m = mass of planet referred to sun.
k and k' are constants adjusted so that the effect for the earth is unity.
s = angular diameter of planet, measured in seconds of arc, as seen at its mean distance from sun.

result depends on the number of electrons ejected by the sun and caught by the planet, we might expect the effect to diminish rapidly with distance. But if Jupiter exerts an influence comparable with that of Mercury the law of

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action can hardly diminish more rapidly than according to the inverse third power. If Jupiter has an effect, mass or size must come into play. I have added the last column to show the relative position of the planets with regard to their size and distance, irrespective of mass.

The Production of Characteristic Röntgen Radiations.

By R. WHIDDINGTON, B.A., St. John's College, Cambridge.

(Communicated by Sir J. J. Thomson, F.R.S. Received April 29,—Read May 25, 1911.)

We know from the researches of Barkla and Sadler and others that many of the phenomena in connection with the emission of secondary Röntgen rays can be explained quite simply by supposing that there are two distinct ways in which matter subjected to the action of primary rays may itself become a centre of radiation :—

(1) The primary rays may be scattered—an effect which is always very small.

(2) The primary rays may be transformed into a type of radiation characteristic of the transforming material and re-emitted as such.

This latter type of secondary radiation has been variously termed "characteristic," "homogeneous," "fluorescent." Each of these terms is expressive, but the first is perhaps the best, and will be used below.

The more important points in connection with the production and properties of this type of radiation are as follows :—

(1) A characteristic radiation is homogeneous or nearly so.

(2) It is only when the primary rays contain a constituent more penetrating than the characteristic to be excited that the stimulation can be effected (whence the term "fluorescent").

(3) The penetrating power of a characteristic radiation increases with the atomic weight of the emitting element.

(4) The characteristic radiation is invariably accompanied by emission of corpuscles from the surface of the radiator.

The experiments to be described have to do with (2) and (3), and define the quality of the softest primary radiation which can stimulate a characteristic, in terms of the velocity of the cathode rays within the exciting X-ray tube. The experiments consist broadly in directing a stream of cathode

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rays of known velocity and intensity on to an anticathode, the primary Röntgen rays so produced falling on a secondary radiator. So long as the cathode rays possess a velocity less than a certain critical value (v_c) no characteristic rays are emitted, but above this speed they become appreciable.

The values of v_c for the radiators Cr, Fe, Ni, Cu, Zn, and Se have been determined in this sort of way.* The value of v_c for Al has been already given.†

The Apparatus.

The first experiments were performed with very simple apparatus, the velocity of the cathode rays being deduced from the length of the equivalent spark-gap when the tube was running. It was soon found, however, that

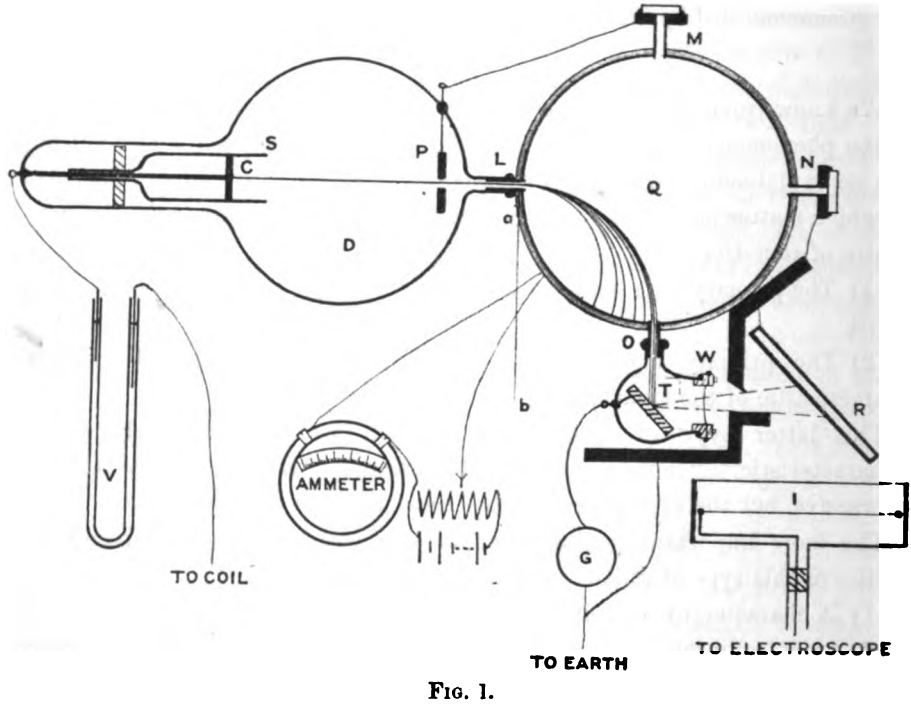

FIG. 1.

beyond the fact that many of the characteristic radiations came in at velocities corresponding to potentials of about 10,000 volts, no more information could be obtained.

The form of apparatus finally adopted is indicated in fig. 1. It is perhaps not worth while to give in detail all the advantages of this particular form

* Preliminary results have been published in the 'Camb. Phil. Soc. Proc.,' 1911, vol. 16, p. 150.

† Whiddington, 'Roy. Soc. Proc.,' A vol. 85, p. 113.

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of apparatus; I may say, however, that an induction coil* is far more satisfactory to work with than the most recent form of influence machine (the Mercedes). The method consists in producing cathode rays in the ordinary way in a vacuum tube, spreading them out into a "magnetic spectrum," and sifting out the required velocity through a suitably placed aperture.

D is a discharge tube fitted with the hardening device I have described to the Cambridge Philosophical Society.† By it the velocity of the cathode rays from C can be instantly changed to almost any desired value *without altering the gas pressure.* This bulb D furnishes a strong source of cathode rays, and is connected at L to a brass cylinder Q (shown in cross-section). L, M, N, and O are co-planar brass tubes 3 mm. in internal diameter, any pair of neighbouring tubes being at right angles. The cylinder Q is closed at each end and made vacuum tight; it is wound on the outside with four layers of No. 16 cotton-covered copper wire in solenoid fashion. The length of the cylinder is 35 cm., its diameter 10 cm.

When a current traverses the solenoid a very uniform and sharply bounded magnetic field is set up within the cylinder. A high "dispersion" can be effected in this way with very moderate exciting currents, the individual rays describing circles with centres on *ab.* It must be mentioned, however, that owing to the finite length of Q there is a small, but appreciable, magnetic force set up outside it when a current passes round the solenoid. This can easily be balanced out by means of a few turns of wire suitably placed, and in series with the solenoid.

The tubes M and N are for "sighting," and are closed at their ends with pieces of plate glass. The inside of Q is sprinkled with finely powdered Willemite so that the places struck by the cathode rays can be visually observed. The glass tube T is about 3 cm. in diameter, and contains a silver anticathode inclined as shown and mounted opposite a thin aluminium window W, through which the Röntgen rays escape. The inside of T is slightly silvered and metallically connected to the anticathode, which in its turn is joined to earth through the galvanometer G. The tube T thus functions as a Faraday cylinder, the reading of G giving the current carried by the cathode rays entering T, their velocity being given by the reading of the ammeter (since only those rays which are bent through a right angle can enter T).

R is a secondary radiator placed opposite the window W, and also opposite the ionisation chamber I, connected in the usual way to a Wilson tilted electroscope.

* A Cox mechanical interrupter was used in preference to a mercury break.

† *Loc. cit.*

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Now in these experiments the energy in the secondary rays measured in I is only a very small fraction of the energy in the primary rays striking R; the energy in these primary rays is again only a small fraction of the energy in the cathode rays striking the anticathode. It is therefore of great importance to make use of the largest possible fraction of the cathode rays emitted by C. The velocity-number distribution of the rays is given in fig. 2A, which is typical of the many curves at all sorts of velocities which have been obtained. It is very convenient that there should be such a considerable concentration of the rays into the highest velocity end of the spectrum; since, by setting this maximum on the centre of O, one not only makes use of the largest possible number of cathode rays, but, at the same time, one fulfils the condition necessary for their greatest possible homogeneity, a point which will now be gone into in more detail.

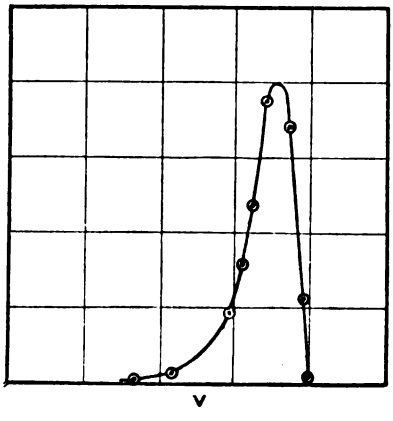

Fig. 2A.

Fig. 2B represents an imaginary spectrum distribution in a beam of rays 3 mm. wide (on emerging from L) as analysed by a very fine aperture at O. There is an apparent range of velocities in this flat-topped maximum corresponding to its width *pq*; but the thick-line curve may be regarded as made up of a large number of smaller similar curves contributed by the different elements of the aperture L. The actual velocity of the rays included in the

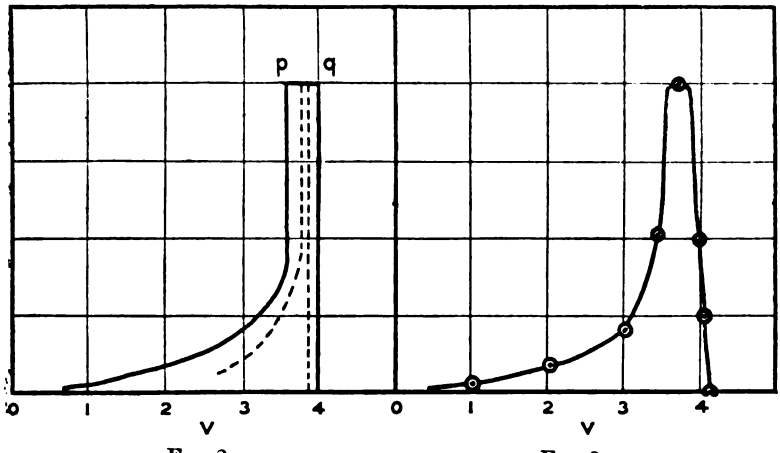

Fig. 2B. Fig. 2C.

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apparent range pq will be that corresponding to the central element (represented by the dotted curve).

Now the distribution in fig. 2B, if analysed by an aperture 3 mm. wide at O, would give the apparent distribution of fig. 2C—a curve very similar to that experimentally obtained (fig. 2A). It is therefore allowable to use the imaginary curve of fig. 2B (which gives a close approximation to the true distribution) to estimate the constitution of the rays entering T.

It comes out that when the maximum of the curve falls on the centre of O, 70 per cent. of the rays entering T have a velocity v (corresponding to the rays entering at the centre of O and coming from the centre of L), while the remaining 30 per cent. have velocities ranging between v and $0{\cdot}955v$. If there had been an impartial distribution in the spectrum and O were placed in the middle, then the rays entering T would have possessed velocities ranging *continuously* between about $1{\cdot}045v$ and $0{\cdot}955v$.

A few remarks are necessary as to the calculation of the velocity of the rays from the strength of the current in the magnetic solenoid.

The formula connecting the radius r of the circular path described by a particle of mass m and carrying a charge e in a uniform magnetic field of strength H is

$$v = \mathrm{H}.r.e/m, \quad \text{where} \quad e/m = 1{\cdot}77 \times 10^7 \text{ E.M.U.} \qquad (1)$$

In this particular case r is invariable and very nearly equal to the mean radius of the solenoid producing the magnetic field. H on the other hand is variable, its value depending on the current (c) in the solenoid. The relation $\mathrm{H} = gc$ gives the connection between H and c, the constant g depending on the shape and winding of the solenoid. It is not altogether satisfactory to rely on the value of g found from a formula, since in addition to the solenoid having a finite (and not accurately known) length, it has a gap in the middle through which the tubes L, M, N, and O pass. The value of g was therefore determined experimentally by measuring H with a search coil and galvanometer. As a matter of fact g found in this way differed only slightly from the value calculated from the dimensions of the solenoid.

g was found in yet another way, or what amounts to the same thing, a direct connection between c and v was obtained. The method was to produce homogeneous cathode rays with an influence machine at a potential V, noting at the same time the current c required to deflect them through a right angle to O. The velocity of the rays is obtained from the relation

$$\tfrac{1}{2}mv^2 = e.\mathrm{V}.$$

v found in this way differed by not more than 1 per cent. from that got by calculating H from the formula $\mathrm{H} = gc$, and substituting in (1).

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This must mean, of course, that in this apparatus the cathode rays really fall through the whole potential V.

It is convenient to conclude this description of the apparatus with a brief account of the instruments used.

The Ammeter.—A Weston instrument reading up to 5 ampères in steps of 0·05. It could be read by estimation to 0·005 ampère.

The Galvanometer.—A dead beat instrument of the d'Arsonval type giving one division deflection for 10^{-7} ampère.

The Electroscope.—A Wilson tilted instrument giving 45 eyepiece divisions per volt. The capacity of the whole system was about 8 cm. It was connected to a variable multiple plate air condenser, by means of which the capacity could be increased to 100 cm., or to any of four intermediate values. By this means the sensibility could be suited to the charge to be measured without the trouble of altering the tilt of the instrument.

The Experiments.

The first experiment was to see how the actual primary Röntgen ray energy (E_p) escaping through W depended on the velocity v of the cathode rays striking the anticathode. To do this the radiator R was replaced by the ionisation chamber I. After correcting the observed values of the ionisation currents for the variations of the absorption coefficients of the Röntgen rays with v, it comes out that E_p (per unit cathode ray current) is nearly proportional to v^4, a result deduced theoretically by Sir J. J. Thomson some years ago).* Further experiments have been carried out in this connection which cannot fitly be given here.

To turn now to the emission of secondary rays by radiators placed in the path of this primary radiation. Some of the results are given graphically in fig. 3.† v^4 is measured along the x axis, while E_s, the secondary energy observed in I, is measured along the y axis.

For the sake of clearness, only the curves for the radiators Cr, Cu, and Se are there shown. Exactly similar curves obtain for Fe, Ni, and Zn.

The following table (p. 330), copied direct from the laboratory note-book, indicates the method of taking observations.

The product itk' gives a number inversely proportional to E_s. The mean of some five or six sets of results such as the above go to the making of a single curve.

* "The Electrical Origin of Radiation," 'Phil. Mag.,' August, 1907.

† These curves are not all drawn to the same scale.

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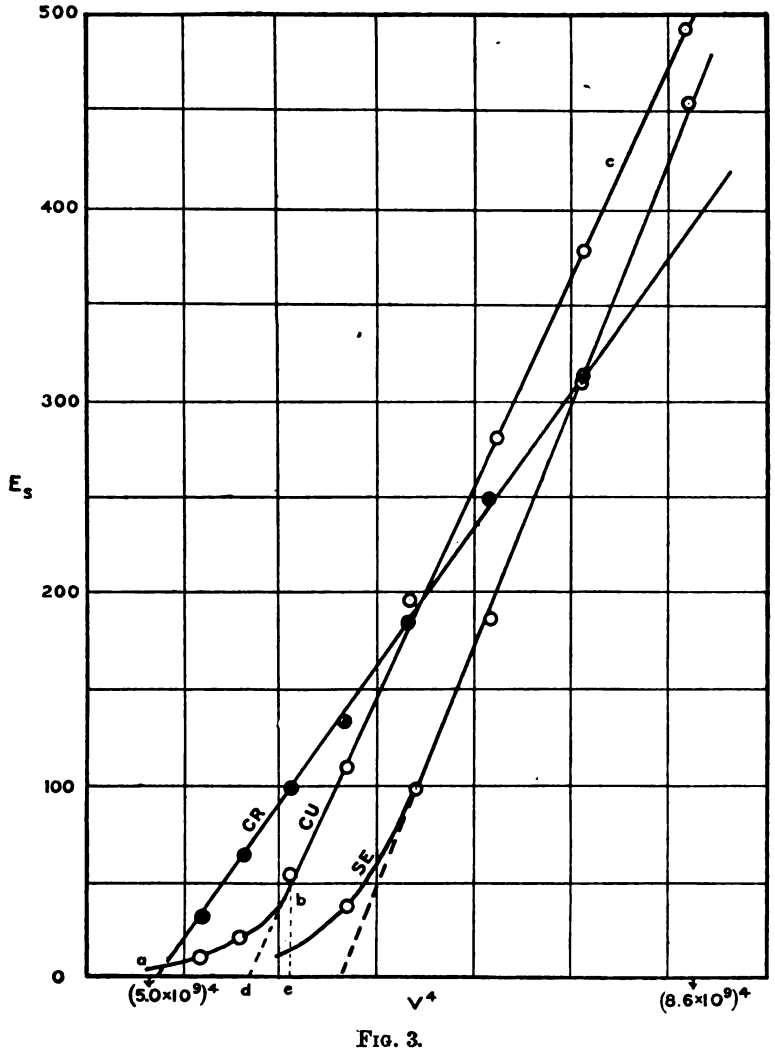

FIG. 3.

The curve for Cu is typical. It is seen to consist (fig. 3) of two parts *ab* and *bc*, having very different slopes and a fairly sudden transition point at *b*. The part *ab* represents quite small values of E_s (see above table), and there is no reason to suppose that it is a straight line, since it must be due to scattered radiation, whose absorption coefficient is diminishing as *v* increases. The part *bc*, on the other hand, is obviously a straight line, and is due almost entirely to the very intense characteristic radiation emitted by R after the point *b* has been passed. (This was proved by measuring the absorption of the rays in aluminium, and comparing with the values given by Barkla and Sadler.) It may be pointed out in passing that

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theoretically one might have expected *bc* to have been somewhat concave to the x-axis, on the assumption, that is, that E_s is proportional to E_p.

Cu radiator.

c.	i.	d.	t.	k.	itk'.	E_s.
2·80	20·0	10	128·0	0	2560	21·5
3·00	20·0	10	57·5	0	1150	47·8
3·20	22·0	10	25·0	0	550	**100**
3·40	30·0	10	27·6	3	248	222
3·60	16·0	10	28·7	3	138	398
3·80	14·0	10	23·4	3	98·0	562
4·00	9·0	10	27·0	3	72·8	758
4·20	7·0	10	26·6	3	55·8	990

In this table—

c = the current in the solenoid.

i = the cathode ray current (the reading of G).

d = the number of microscope eyepiece divisions travelled by the gold leaf in the mean time t.

k = the number denoting the capacity used on the leaf.*

E_s = the secondary energy emitted by R per unit cathode ray current entering T (fig. 1).

It is now necessary to consider the best way of obtaining the position of the point b. If cb be produced, it will cut the x axis in d. In the absence of the part ab of the curve, this point d would give accurately the critical value v_c^4. As it is, however, this gives too small a value. The true value must lie between od and oe. The only method available seems to be to take the mean $\frac{1}{2}(od+oe)$ as giving the best possible value of v_c^4. If, in applying this correction, an error so large as 4 or 5 per cent. be introduced, it will only mean an error of about 1 per cent. in v_c.

The following table gives the results :—

* To the capacity designated by k corresponds a factor k' such that if t is the time taken by the leaf to traverse d divisions when connected to the capacity k, tk' is the time it would have taken to perform the same journey had it been connected to the standard capacity 0. Thus, in this table $k' = 0{\cdot}300$ for capacity 3 which means that a time of (say) 10 seconds with this capacity would reduce to only 3 seconds for the standard capacity 0.

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Radiator.	V_c.	$v_c \times 10^{-9}$.	Atomic weight.	m.	λ/ρ.*
Al	1200	2·06	27·0	—	580
Cr	7320	5·09	52·5	10·0	136
Fe	9600	5·83	56·0	30·0	88·5
Ni	10750	6·17	58·6	46·5	59·1
Cu	11080	6·26	63·2	59·1	47·7
Zn	11280	6·32	65·1	72·7	39·4
Se.....	15400	7·38	78·9	91·0	18·9

* These values of λ/ρ, with the exception of that for Al, are taken from a paper by Barkla and Sadler, 'Phil. Mag.,' 1908.

In this table—

v_c = the critical cathode ray speed.

V_c = the corresponding potential in volts, *i.e.*, that potential above which an ordinary X-ray tube supplied with a steady voltage would have to run, in order to excite the radiation characteristic of the element placed in the same line in the table.

m = the slope in arbitrary units of the straight line representing the connection between E_s and v^4.

λ/ρ = the absorption coefficient of the radiation concerned.

[Particular reference must be made to Al, which figures in the above table. In the paper referred to above, evidence was brought forward indicating that Al does not obey the "fluorescence law" to which the elements studied by Barkla and Sadler certainly conform. This would explain the rather low value of v_c.]

The above table shows that, at any rate, an approximate linear relation exists connecting v_c and the atomic weight.*

It was not possible to work with cathode rays moving faster than about 10^{10} cm./sec., on account of the difficulty of making the tube run steadily; up to this velocity, however, the radiation characteristic of silver could not definitely be detected.

The Cr curve in fig. 3 was obtained, using a radiator made of the pure element. I have tried a radiator consisting of a plane plate of sodium bichromate and have found that both v_c and m are the same as for the element within experimental error.

Experiments on the emission of corpuscles by secondary radiators are now in progress. It seems advisable to reserve discussion of the above results until these experiments be concluded.

* If hydrogen emit a characteristic radiation conforming to this law, the values of v_c and V_c would be 10^8 cm./sec. and 2·82 volts respectively.

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Summary of Experimental Results.

(1) The energy emitted in the form of Röntgen radiation by a cathode particle when suddenly stopped is proportional to the fourth power of its velocity.

(2) The primary rays from a Röntgen ray tube can only excite the radiation characteristic of a radiator of atomic weight w when the velocity of the parent cathode rays exceeds $w \times 10^8$ cm./sec.

This law holds fairly closely for the radiators Al, Cr, Fe, Ni, Cu, Zn, and Se.

It gives me pleasure to thank Prof. Sir J. J. Thomson for the interest he has taken in these experiments.

Experiments on the Compression of Liquids at High Pressures.

By the Hon. C. A. Parsons, C.B., F.R.S., and S. S. Cook, B.A. Cantab.

(Received May 10,—Read May 25, 1911.)

1. *Introduction.*

During the experiments on the behaviour of carbon under high pressures and temperatures, of which an account was given in the paper read before this Society by the Hon. C. A. Parsons on June 27, 1907, very considerable volumetric compressions were observed, and the apparatus then employed appeared to be equally suitable for the direct measurement of the compressibility of liquids at higher pressures than had previously been attempted.

The measurement of the compressibility of liquids has received the attention of a great many investigators; the most comprehensive researches in this subject appear to be those of Amagat, who determined the coefficients of compressibility of water and ether for pressures up to 3000 atmospheres and for a variety of temperatures. Amagat's experiments are given in various numbers of 'Comptes Rendus.'* In the experiments about to be described, the pressures were carried up to about 40 tons per square inch, or over 6000 atmospheres.

* 'Comptes Rendus,' vol. 103, p. 429; vol. 105, p. 1120; vol. 107, p. 522; vol. 108, p. 228; vol. 111, p. 871.

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The experiments were commenced in 1908, but, the first experiments showing some modification of the apparatus to be desirable, principally with a view to making temperature measurements, it is the results of the later experiments carried out during the last year that are chiefly given. A brief reference is desirable, however, to the preliminary readings obtained, by way of explaining the method adopted to eliminate friction, and in order to indicate how these experiments suggested an extension of the research to the investigation of the effects of internal molecular forces of the liquids tested.

2. *Apparatus.*

The apparatus consisted of a steel mould of about 4 inches bore and 12 inches external diameter, placed under a heavy hydraulic press, capable of exerting a pressure of 2000 tons, with a main ram of 29 inches diameter and a 6-inch lifting ram. In the first series of these experiments the mould was constructed of gun steel, having an elastic limit of about 40 tons per square inch. Greater strength could have been obtained, and still higher pressures applied, by the employment of special steel with a higher elastic limit.

Water was supplied to the upper side of the ram at pressures up to 2000 lbs. per square inch by a three-throw hydraulic pump driven by an electric motor. The pressure on the ram was recorded by a carefully calibrated Bourdon gauge, and the depression of the liquid in the mould measured by a pair of multiplying callipers, inserted between the top of the mould and a projecting collar on the plunger. One of the outer arms of the callipers moved over a graduated scale attached to the other arm, and the readings of this scale were for safety observed through a telescope outside the armoured building in which the press and mould were set up. A sketch of the apparatus is given in Diagram I, fig. I. Between the plunger and the liquid was placed a leather cup backed by a thin-edged cup of brass, this combination making an effective packing (see Diagram I, fig. II).

3. *Elimination of Errors.*

In such an apparatus certain errors would arise in a single experiment, but the experiments were carried out in such a manner as to practically eliminate them. The sources of error were the friction of the packing, the compression of the cup leather and brass and of the plunger below the point of measurement, and the lateral expansion of the mould. All these, with the exception of that due to friction, would be eliminated if an experiment could first be made with the mould filled with an incompressible fluid, and the apparent

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DIAGRAM I.

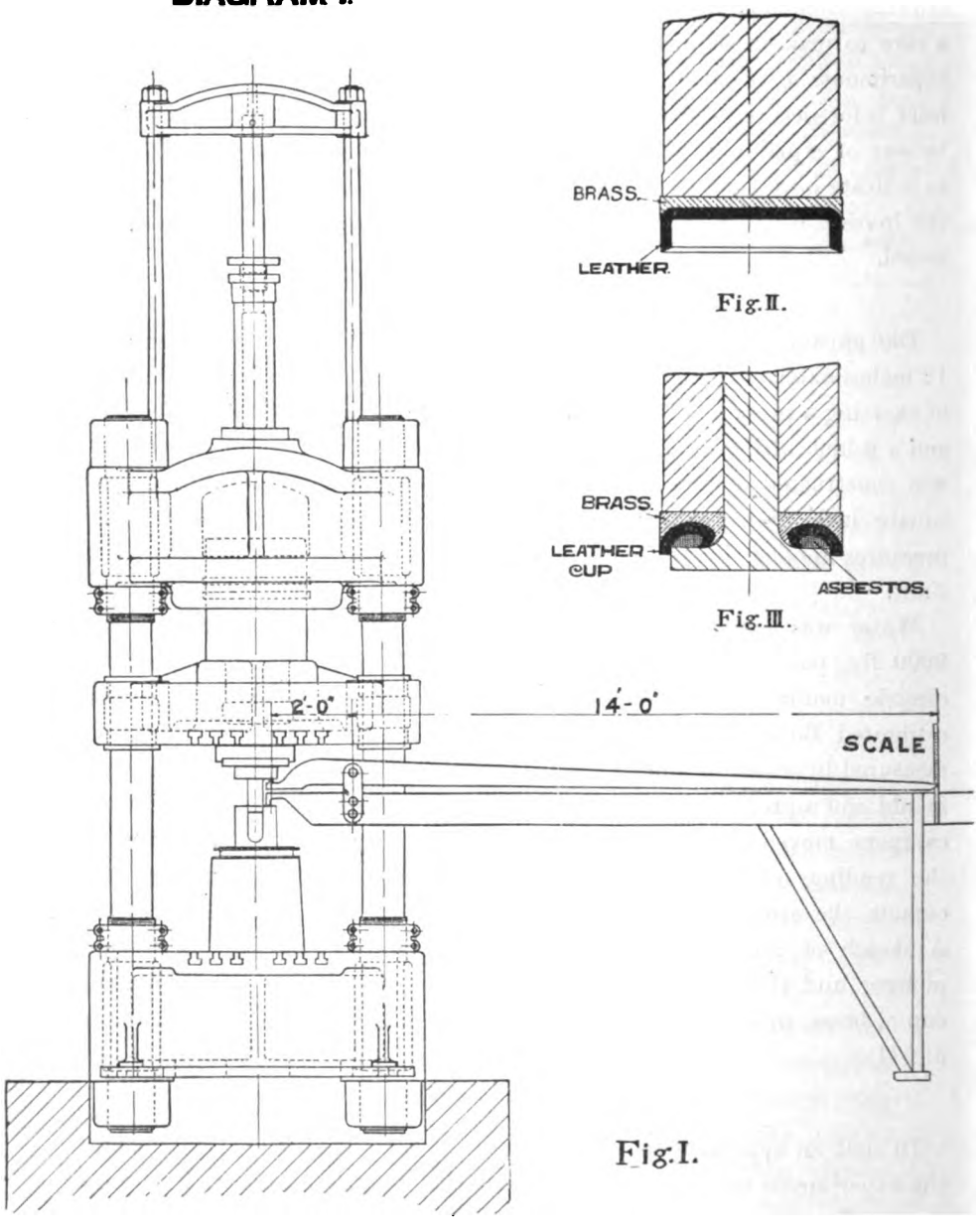

Fig.II.

Fig.III.

Fig.I.

compressions so obtained deducted from those obtained in any other experiment. But as there was no suitable fluid of negligible compressibility, in order to obtain in an indirect manner the apparent bulk compression in this apparatus of a substance of negligible compressibility, the following pro-

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cedure was adopted. A steel cylinder was prepared of half the volume of the liquid and of smaller diameter than the bore of the mould. In a first experiment this steel cylinder was inserted in the mould, which was then filled with distilled water up to a mark corresponding to a total volume of 2000 c.c., so that it then contained 1000 c.c. of water and an immersed volume of 1000 c.c. of steel, both of which could be subjected together to bulk compression, and the apparent compression observed. A second experiment was then made with the steel cylinder removed, and the mould filled to the same mark with 2000 c.c. of distilled water, the apparent compression being read as before.

Since the volumetric compression of the water in the first experiment is only one-half of its value in the second (the original volume of the water compressed being only one-half), by subtracting the compression readings of the second experiment from twice those of the first, the compression of the water is eliminated, and the difference thus obtained gives the constant error of the apparatus on the supposition that the inserted steel cylinder is incompressible.

A small correction is then necessary for the compression of this steel cylinder. The coefficient of compressibility of steel at ordinary pressures, as deduced from the modulus of rigidity and Young's modulus, by the usual formula for the relation between the moduli,* is $0{\cdot}78 \times 10^{-6}$ per atmosphere of pressure. Since this is only a small percentage of the compressibility determined below for water, etc., the reduction in volume of the steel cylinder under a pressure of p atmospheres may be assumed, to a near enough approximation, to be cp times its original volume, where $c = 0{\cdot}78 \times 10^{-6}$. In estimating the compressibility of water by the difference between the apparent compressions obtained in the two experiments, it is obvious that it is greater by approximately this amount (viz., $0{\cdot}78 \times 10^{-6}$) than it would be on the assumption of absolute constancy of volume of the immersed steel cylinder.

A further small correction has been necessary owing to the expansion of the mould taking effect upon slightly different volumes in different experiments. This correction has been estimated by the usual theory of the bursting strains of thick cylinders, its magnitude at the highest pressures employed never exceeding 1 per cent.

4. *Elimination of the Effects of Friction.*

Curve 1 gives the readings without corrections obtained with the mould containing 2000 c.c. of distilled water at 18° C. The vertical ordinate

* See Thomson and Tait's 'Natural Philosophy,' § 683.

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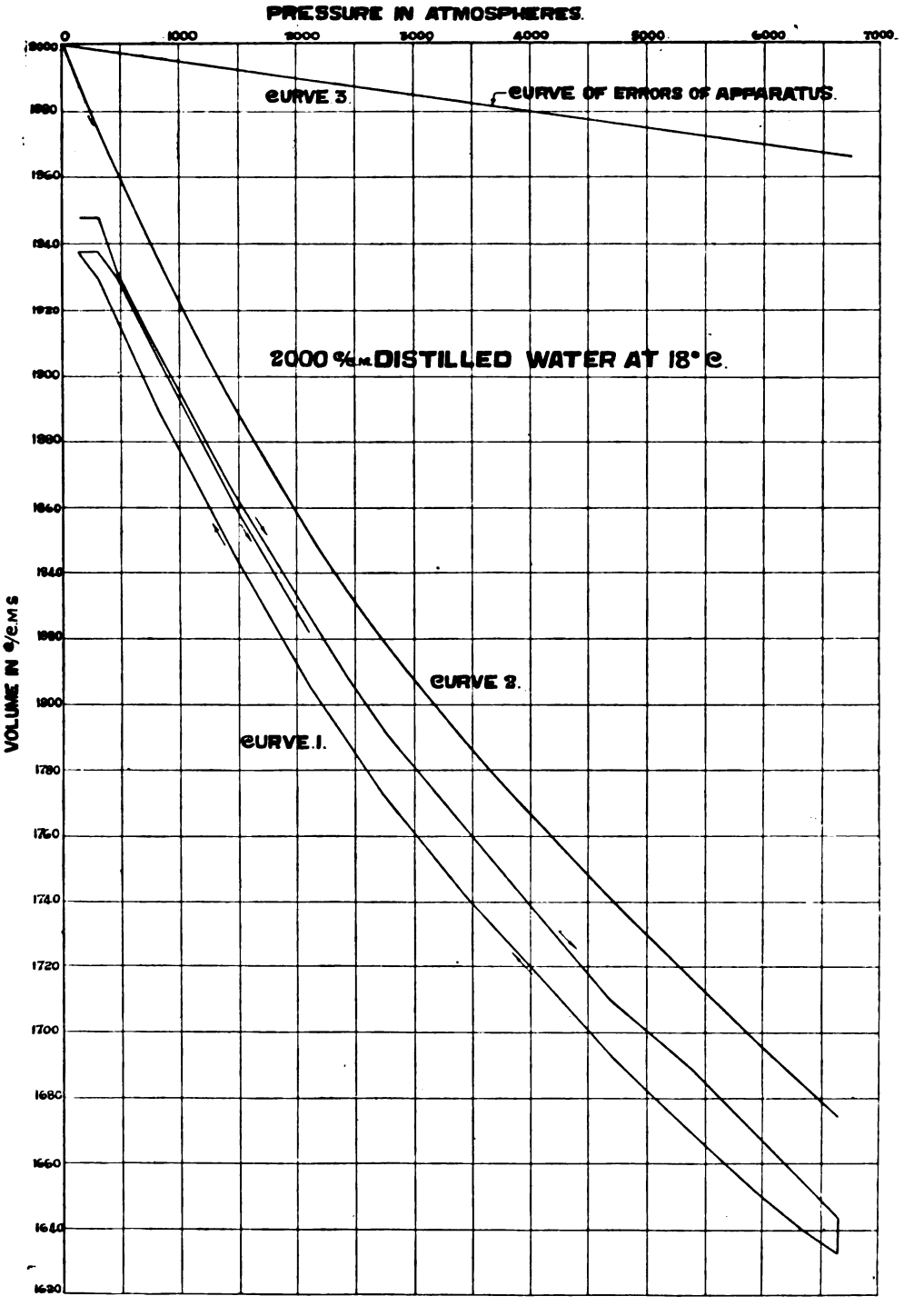

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represents the volume of the liquid as indicated by the depression of the plunger, and the abscissa the pressure in atmospheres.

The cyclic nature of the curve will be noticed, the upper branch of the loop being plotted from the readings obtained when the pressure was increasing, and the lower from those obtained whilst the pressure was being reduced; the difference between the readings of the upper and lower branches is concluded to be due to friction, the horizontal breadth of the loop being twice the pressure needed to overcome the friction of the packing and of the working parts of the press.

Loops of this nature were traced for all the experiments. To guard against leakage, after the pressure had been raised to its highest value and reduced back to zero, it was again raised so as to repeat a portion of the higher branch of the loop; if any leakage had taken place it was thus at once detected, and the experiment rejected.

By drawing a curve midway between the two branches of the loop we obtain a curve of compression with the effects of friction eliminated. Curve 2 is the curve plotted for 2000 c.c. of water in this manner. Curve 3 is a curve of errors of the apparatus obtained by a calibrating experiment with the immersed steel cylinder as described above.

Curve 4 gives readings plotted for a heavy cylinder oil of mean density about 0·89 at 20° C. It will be noticed that the loop of Curve 4 is very similar to that for water, Curve 1, in spite of the greater viscosity of the oil, so that it would appear that the loop obtained in all the experiments with liquids is entirely due to friction of the press and packing, and not to internal friction.

5. *Behaviour of Graphite under Pressure.*

Similar measurements were attempted with powdered Atchison graphite of specific gravity 2·23 and containing 2¾ per cent. of ash. The readings obtained are plotted in Curve 5. It was thought possible that under high pressure graphite would behave as a fluid, but the character of the curve obtained indicates an increasing degree of consolidation as the pressure is increased. The consolidated graphite appears to show considerable rigidity, that is to say, the stress was not equal in all directions. The lower portion of the cycle was repeated, applying and removing the pressure a great number of times, the dotted Curve 6 representing the readings subsequently obtained.

On opening up the mould the graphite was removed in biscuit-like fragments, often separating along a conical surface at about 45° to the axis, so that it appears to have relieved itself during expansion along lines of cleavage at this angle.

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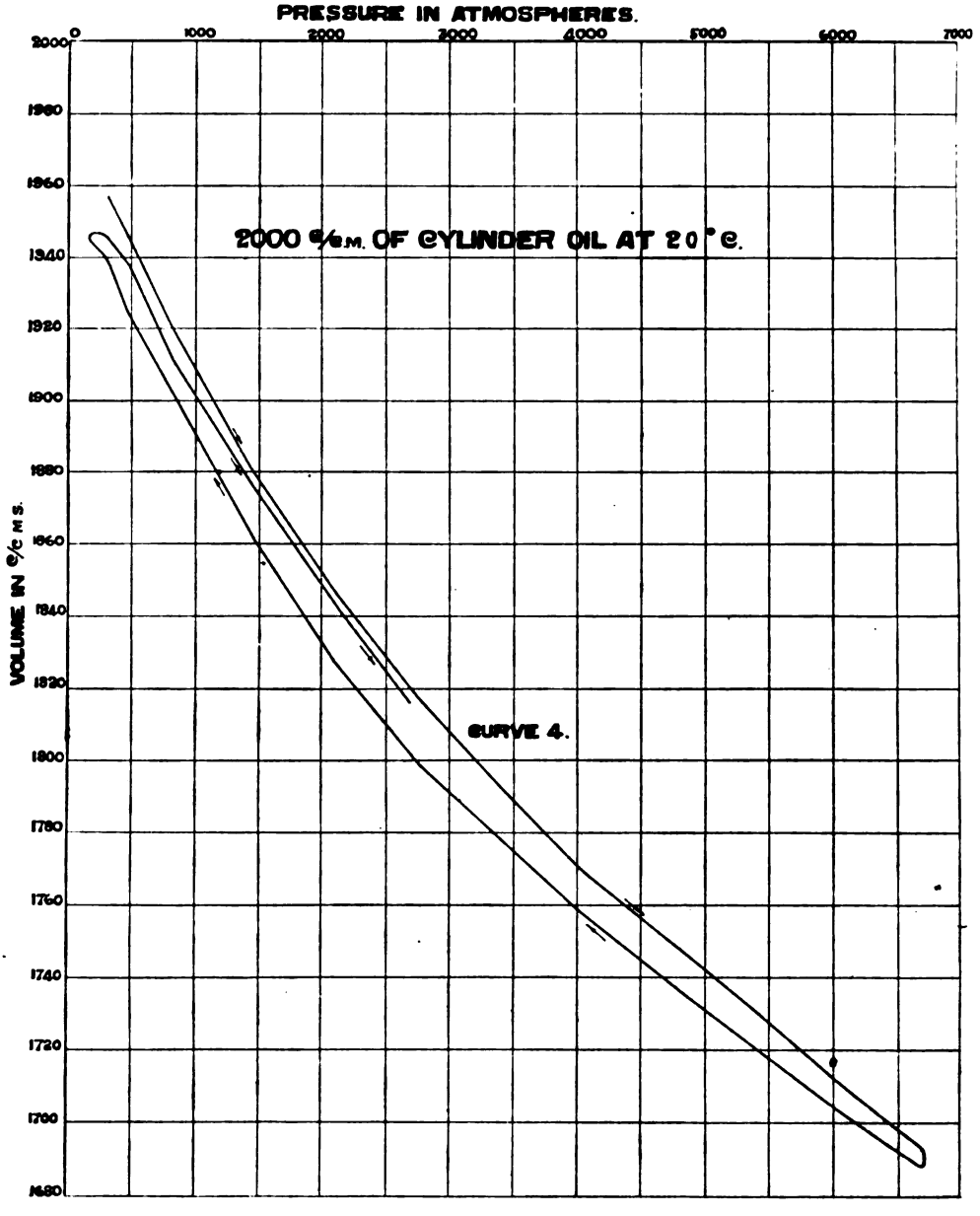

From these results it was difficult to conclude whether the graphite had undergone much bulk compression. The bulk compressibility was, however, subsequently determined by the compression of 1400 grm. immersed in 1300 c.c. water, and was found to be about $6{\cdot}5 \times 10^{-6}$ in atmospheric units. Curve 7 is a curve of bulk compression deduced in this manner for

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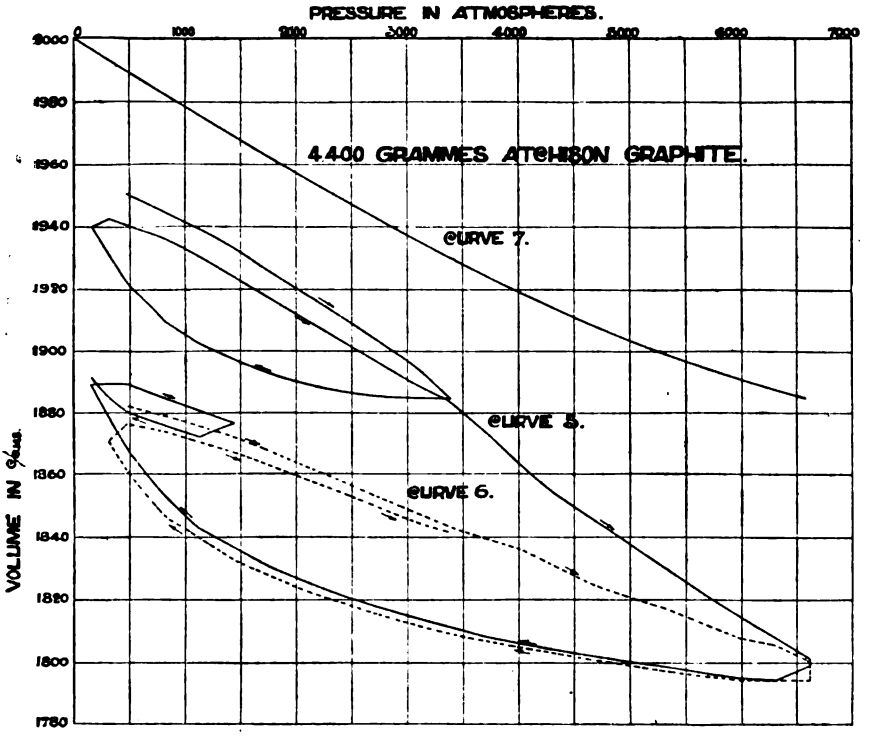

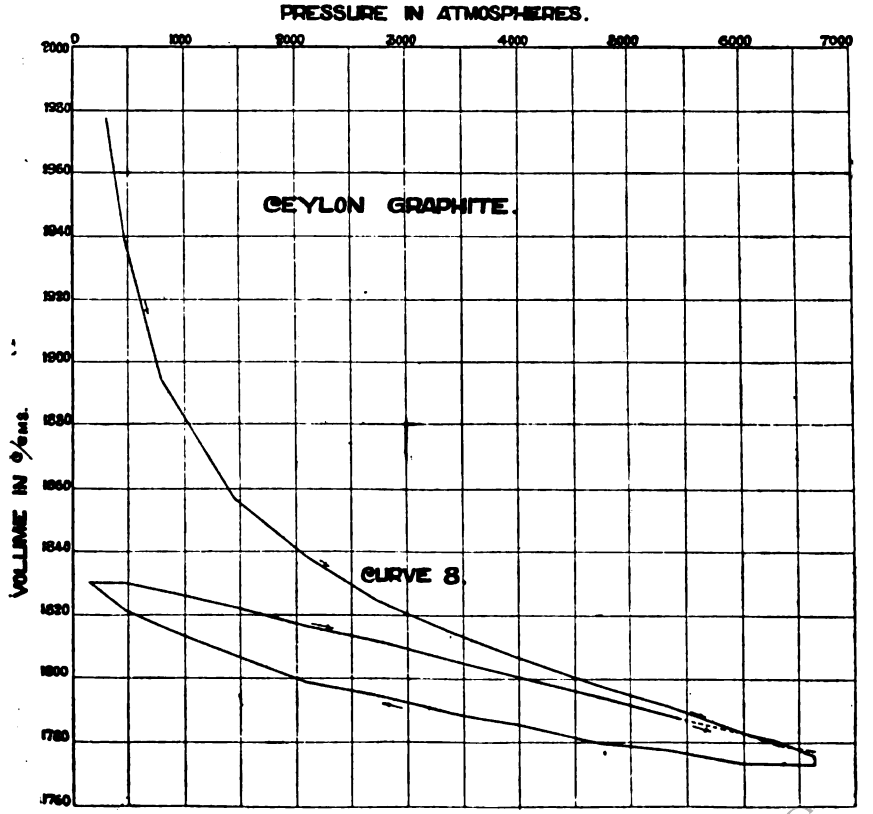

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comparison with Curve 6, and, as will be seen, is nearly parallel to the upper branch of the loop.

Similar results were obtained with Ceylon graphite of specific gravity 2·3 and containing about 15 per cent. of ash. The readings for this graphite are plotted in Curve 8.

6. *Effects of Heat of Compression.*

It will be observed that in the curves plotted for the experimental readings, the readings for the pressures ascending a second time for the purpose, as explained above, of detecting leakage, are in general very slightly below the readings for the previous application of the pressure. Subsequent examination of the apparatus showing no trace of leakage, and this phenomenon persisting in subsequent experiments, it was concluded to be due to temperature variation, the work done during compression transforming into heat and rendering the substance, whilst under high pressures, slightly hotter than its surroundings, so that at the end of the cycle it had lost some heat to the surroundings, and during the second compression was slightly colder than during the first. This heat effect being therefore a possible source of error, it was desirable to make some measurement of its amount.

As a preliminary, a volume of 2000 c.c. of heavy cylinder oil was compressed to a pressure of 6300 atmospheres, which was maintained for two hours to allow the heat due to compression to leak away. At the end of this time the pressure was suddenly released, and the liquid was found to be 1/5 inch lower in the mould than it was before compression, corresponding to a reduction in total volume of about 2 per cent.

The heat effect was further investigated by allowing 2000 c.c. of thin machine oil to cool under high pressure for two hours with an external temperature of about 11·5° C., and after sudden removal of the pressure opening up the mould for examination. With the method of packing employed at this time (see Diagram I, fig. II) it was not possible to open up in less than about a quarter of a hour, owing to the difficulty of removing the brass cup and the cup-leather from the mould.

The temperature after opening up was read, however, at regular intervals of time, by which means, assuming a logarithmic law, the temperature immediately after release and expansion could be estimated, and appeared at the moment of release to have been about 24·5° C.

It was evident from this that the loss of heat was considerably in excess of that due to the work done on the piston during expansion. The specific heat of the oil was measured and found to be about 0·5. The temperature reduction, 36° C., which took place corresponds, therefore, to 18 centigrade heat units per lb. The work done by expansion was about 42,000 ft. lbs. for a mass of

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about 4 lbs., which is equivalent only to 7·5 heat units per lb., leaving 10·5 units per lb. to be accounted for by internal forces.

This point having been reached, the experiments were continued with a twofold object, namely, (1) to ascertain the compressibilities of various liquids for both adiabatic and isothermal compression, the experiments last referred to showing it to be necessary to discriminate between these modes of compression, and (2) to determine the amount of the heat developed from internal forces during compression and absorbed by the same agency during expansion.

Various attempts were made to measure the instantaneous temperature of the contents of the mould during compression by electrical methods with platinum coils and terminals brought outside the mould to a galvanometer. None of these were successful; the readings suffered interference from galvanic action and from conduction in the liquid, and constant difficulty was experienced through breakage of the coils with congealed oil and through leakage of the fluid past the terminals, in spite of many precautions taken to avoid these difficulties.

In the meanwhile an accumulator had been installed, and it was now possible to put on or remove the full pressure almost instantaneously; further, by attaching the packing to the ram in such a way that it could be withdrawn immediately on the removal of pressure (see Diagram I, fig. III), it was possible to insert a quick-reading mercury thermometer immediately after release. The mould was also surrounded by a water jacket so that the temperature could be varied as required and measured by a mercury thermometer.

Isothermal curves were plotted by allowing the pressure to remain applied long enough for the liquid in the mould to assume the temperature of the jacket, after which the pressure was varied slightly above and slightly below its recorded value sufficiently to overcome the friction.

For adiabatic compression the pressure was raised to the required value in a few seconds. In these later experiments the pressures were not carried higher than from 4500 to 5000 atmospheres, the adoption of which lower values, together with the experience acquired in working with these high pressures, rendered it safe for the observer to work inside the building close to the apparatus, which greatly facilitated the readings.

7. *Experiments with Water.*

Curve 9 is an isothermal curve obtained for the compression of distilled water at 4° C. plotted to a base of pressure in atmospheres, the vertical ordinates giving the volumes of a kilogramme in cubic centimetres. In the case of water the adiabatic compression was found to be only about

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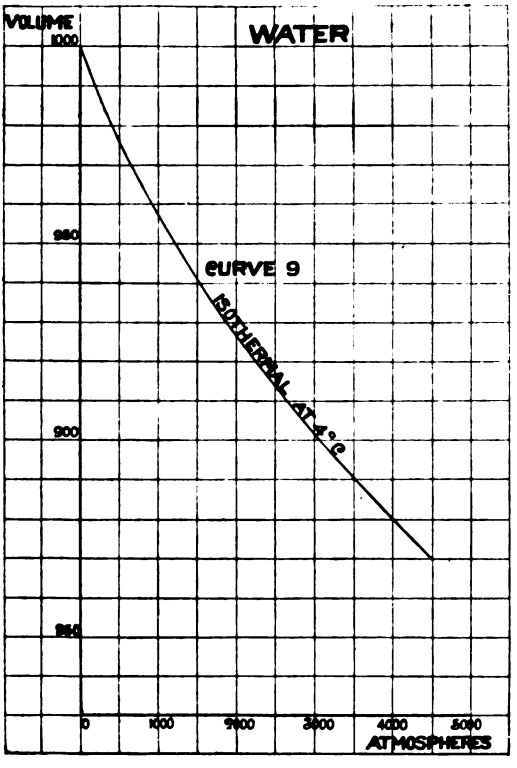
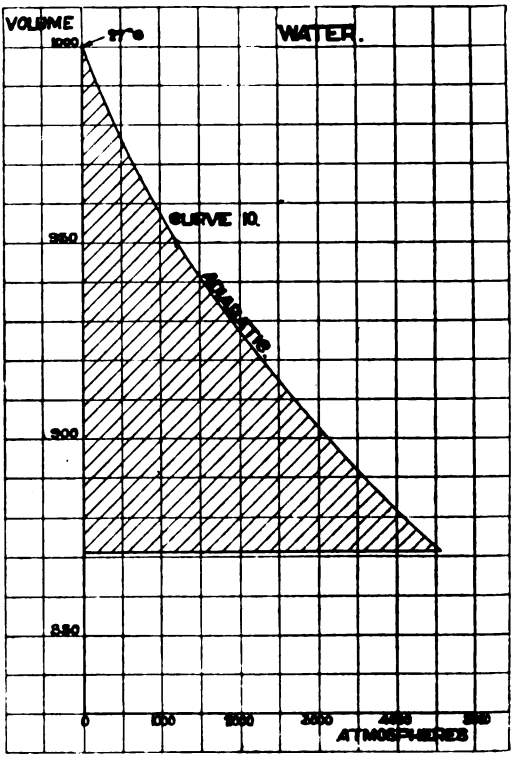
3 per cent. less than the isothermal. With other substances, as will be seen below, the difference was greater, on account of lower specific heat and apparently higher internal forces.

Curve 10 is a curve of adiabatic expansion of water from a temperature of 40° C. at 4550 atmospheres pressure. The temperature at the end of this process of adiabatic expansion was found to be 27° C., so that 13 calories per kilogramme have to be restored to bring the water back to 40° C. at atmospheric pressure. The external work done during expansion is given by the shaded area under the curve and amounts to 2700 kilogramme-metres





per kilogramme. But the 13 calories of heat which have to be added per kilogramme are equivalent to 5500 kilogramme-metres, so that in passing from the initial state of 40° C. temperature and 4550 atmospheres pressure to a final state at the same temperature and atmospheric pressure 2800 kilogramme-metres of energy have become latent, or in other words have been converted into internal potential energy. The increase of volume between these two conditions is 130 c.c., and this disappearance of energy is therefore equivalent to the work that would be done against an internal force of average value = 280,000 ÷ 130, or 2150 atmospheres.

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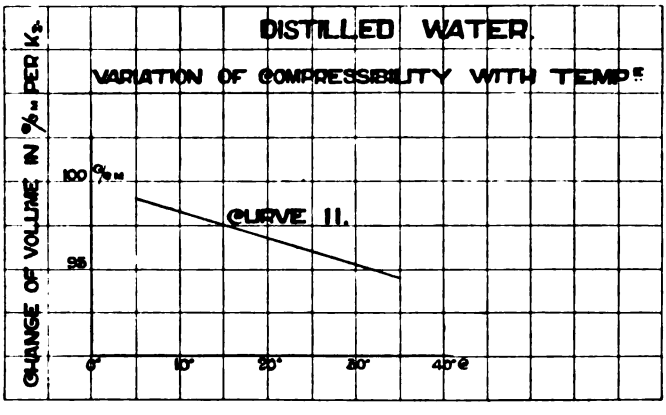
It will be seen that by increasing the pressure from 1 up to 4500 atmospheres water at 4° C. is compressed to 87 per cent. of its original volume. At 3000 atmospheres it is 90·2 per cent. This agrees closely with 89·8 per cent. given by Amagat for 3000 atmospheres pressure at 0° C.

An endeavour was also made in the case of water to find the influence of temperature upon compressibility. For this purpose the water was compressed adiabatically at various temperatures. Readings were taken of the compression at 600 atmospheres and immediately afterwards at 4500 atmospheres, the interval elapsing being only a few seconds. The amount of the compression between these pressures is plotted in Curve 11, the units adopted being change of volume in cubic centimetres per kilogramme for the vertical ordinate and temperature before compression for the horizontal base. The compressibility is reduced with increase of temperature, from



which it follows that the coefficient of heat expansion at high pressures is slightly greater than at atmospheric pressure. This is in agreement with Amagat's results.

8. *Experiments with Ether.*

Curve 12 shows the compressibility of pure ether at 35° C., the vertical ordinate being the volume in cubic centimetres of a quantity whose volume is 1000 c.c. at 0° C. The compression for 4000 atmospheres is from 1050 c.c. to 840 c.c., the final volume being 80 per cent. of the original, so that the compression in this case is practically double that obtained for water. The agreement with Amagat's results in this case also is fairly good, the latter giving a compression from 1050 to 863 for 3000 atmospheres at 35° C., whilst by the present experiments it appears to be from 1050 to 870, the disagreement being only about 4 per cent. of the total compression measured.

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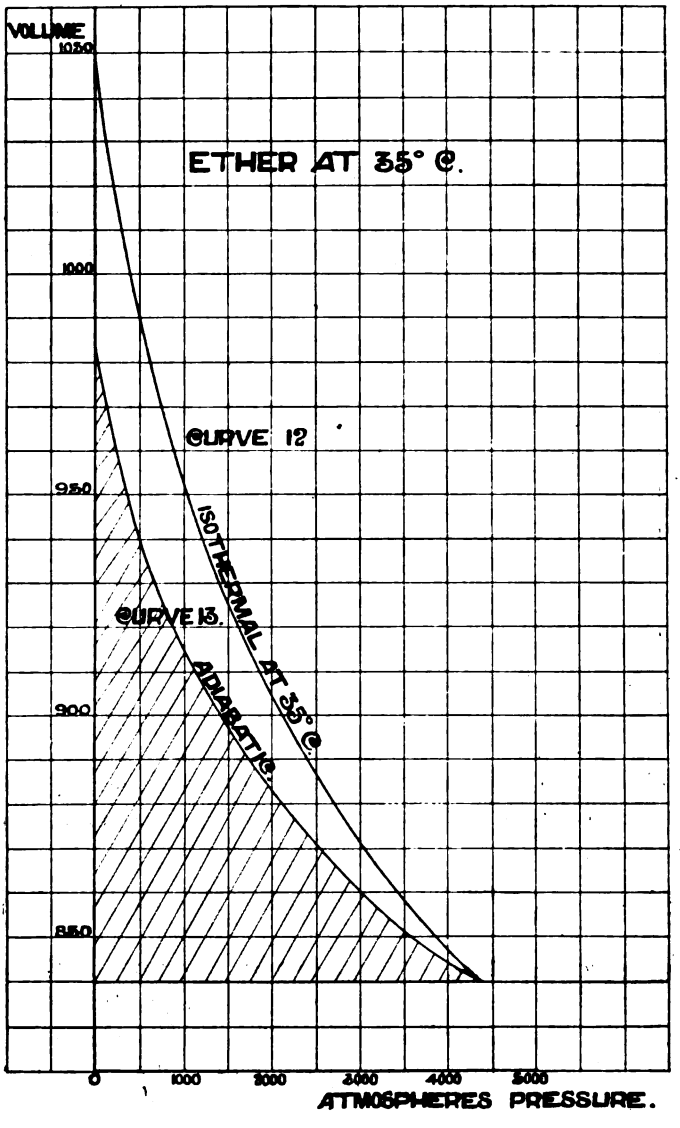
Neither for ether nor for water can the curves showing the results of these experiments be said to definitely indicate the existence of a limiting value to the compression.

In the case of ether, as in the case of water, experiments were made to



ascertain the heat absorbed through the action of intermolecular forces by sudden expansion. Curve 13 is the curve of adiabatic expansion after cooling at 4400 atmospheres to 35° C. The final temperature was −11° C. This drop of 46° C., assuming the specific heat of ether to be 0·516, corresponds

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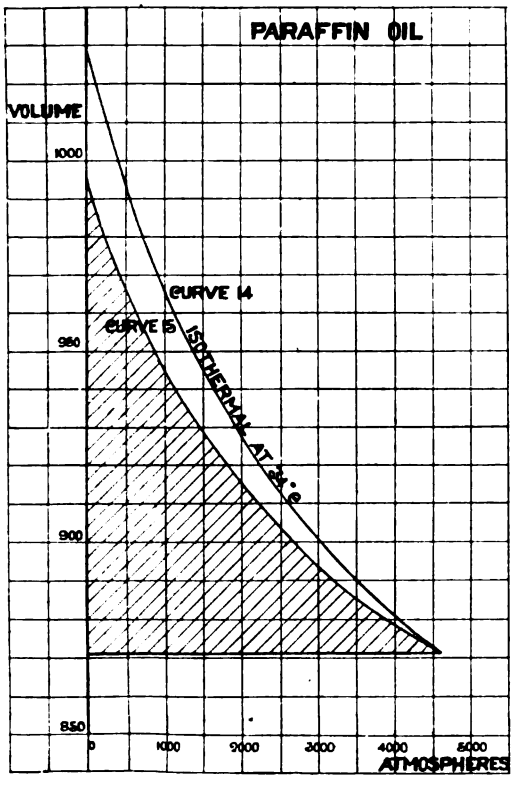
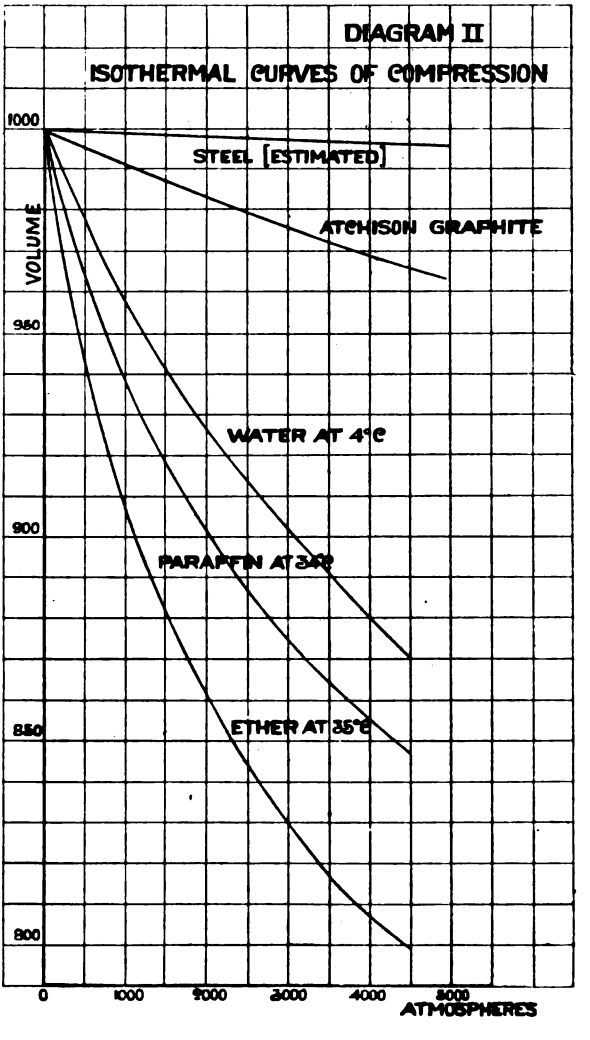
to 7200 kilogramme-metres of energy for unit of volume 1000 c.c. at 0° C. The external work done during expansion is given by the shaded area under Curve 13, and is 2070 kilogramme-metres, leaving for the internal work 5130 kilogramme-metres, representing an average molecular pressure of 2440 atmospheres.

9. *Experiments with Paraffin Oil.*

Curve 14 gives the isothermal compression at 34° C. of a paraffin oil of flash point 131° F., and of specific gravity 0·812 at 0° C., and 0·788 at 34° C., the vertical ordinate being the volume of 812 grm. of the liquid. Curve 15 is the curve of adiabatic expansion after cooling to 34° C. at 4600 atmospheres. With 4500 atmospheres the oil is compressed isothermally





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to 871 c.c., or about 84½ per cent. of its original volume at 34° C.; the compressibility is therefore greater than for water by about 20 per cent.

The drop in temperature on expansion from 4600 atmospheres to atmospheric pressure was found to be 39° C. Taking the specific heat at 0·5, the energy extracted per 1000 c.c. is made up of 2055 kilogramme-metres of external work and 4645 kilogramme-metres work against internal forces, the latter corresponding to a pressure of 2920 atmospheres.

10. *Conclusion.*

To exhibit the comparison between them, the curves of isothermal compression have been replotted in Diagram II, reduced to a common basis of 1000 c.c. original volume.

Expressing compressibility in atmospheric units, that is to say, as the ratio of the decrease of volume per atmosphere of pressure to the volume of the liquid, from the foregoing experiments the following values have been deduced for the isothermal coefficients of compressibility of water, ether, and paraffin oil:—

	Temperature.	Pressure.	Compressibility.
Water	4° C.	Atmospheric	50×10^{-6}
		2000 atmos.	25×10^{-6}
		4500 „	$22{\cdot}5 \times 10^{-6}$
Ether	35° C.	Atmospheric	165×10^{-6}
		1000 atmos.	64×10^{-6}
		2000 „	$42{\cdot}5 \times 10^{-6}$
		4500 „	18×10^{-6}
Paraffin oil	34° C.	Atmospheric	87×10^{-6}
		2000 atmos.	34×10^{-6}
		4500 „	17×10^{-6}

The average values of the molecular force deduced from the heat lost during adiabatic expansion as described above are as follows.—

	Molecular force. atmos.
Water (for pressures between 0 and 4550 atmos.)	2150
Ether „ „ 0 „ 4000 „	2440
Paraffin „ „ 0 „ 4600 „	2920

The authors wish to record their thanks to Mr. Robert Howe for assistance with the mechanical work in connection with the experiments.

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Appendix (*June* 3).

The method adopted in the paper for determining the equivalent internal pressure corresponding to the excess of heat extracted over the external work done is based on the following considerations :—

Suppose a closed cycle on a pressure volume diagram, made up of the following processes in succession—(*a*) isothermal compression at temperature T_1; (*b*) adiabatic expansion to atmospheric pressure and temperature T_2; (*c*) restoration to temperature T_1 by addition of heat at atmospheric pressure.

The external work during process (*c*) is negligible. Hence the excess of the heat given out over external work done during (*a*) can be measured by the excess of the heat absorbed during (*c*) over the external work done during (*b*).

The excess thus determined in (*a*) has been expressed as the product of an average internal pressure into the change of volume occurring during the isothermal compression (*a*).

The rate of rise of temperature of fluids under compression can be determined from the thermodynamic relations resulting from the first and second laws of thermodynamics. When there is no emission of heat, we have with the usual notation

$$0 = K_p d\tau - \frac{\tau}{J}\left(\frac{\partial v}{\partial \tau}\right)_p dp, \tag{1}$$

from which

$$\frac{d\tau}{dp} = \tau\left(\frac{\partial v}{\partial \tau}\right)_p \Big/ JK_p. \tag{2}$$

Using α to denote the coefficient of expansion at constant pressure, or $\frac{1}{v}\left(\frac{\partial v}{\partial \tau}\right)_p$, we have

$$\frac{d\tau}{dp} = \frac{\tau v \alpha}{JK_p}. \tag{3}$$

This formula will ordinarily only bear application in the neighbourhood of atmospheric pressure, the values of α and K_p under the high pressures employed in the foregoing experiments being unknown.

Thus, for the adiabatic curve plotted for water, in the neighbourhood of atmospheric pressure, we have for the various expressions in equation (3)—

$$\tau = 273 + 27 = 300, \qquad J = 42400 \text{ kgrm.-cm. per kgrm.}$$
$$v = 1000 \text{ c.c. per kgrm.} \qquad \alpha = 0{\cdot}00025,$$

from which there results $d\tau/dp = 0{\cdot}00177$, or a rise of 0·00177° C. per atmosphere of pressure. The rise in temperature will, however, in the case of water, proceed more rapidly in the later stages of the compression as higher pressures are reached, since α increases both with the temperature and with the pressure.

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With the help of Curve 11 it is possible to obtain an approximate estimate of the value of α of the fluid when under compression. Denoting by β the compressibility at constant temperature, since

$$\beta = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_\tau \quad \text{and} \quad \alpha = \frac{1}{v}\left(\frac{\partial v}{\partial \tau}\right)_p,$$

it follows that

$$\left(\frac{\partial \alpha}{\partial p}\right)_\tau = -\left(\frac{\partial \beta}{\partial \tau}\right)_p.$$

The slope of Curve 11 gives for the value of $-\partial\beta/\partial\tau$, with the unit adopted for β (viz., change of volume per unit volume per atmosphere of pressure), $0{\cdot}035 \times 10^{-6}$, and if we assume this as the approximate rate of increase of α throughout the range of pressures covered by the adiabatic compression from 27° C. at atmospheric pressure to 40° C. at 4550 atmospheres pressure, we have for the value of α at the beginning of the compression 0·00025, and at the end 0·00061, or an average value of 0·00043.

The expressions in equation (3) then assume the following average values over the whole range of this compression—

$$\tau = 306{\cdot}5, \qquad \alpha = 0{\cdot}00043,$$
$$v = 940 \text{ c.c. per kgrm.},$$

giving $d\tau/dp = 0{\cdot}002925°$ per atmosphere.

The measured drop in temperature during the reverse process of adiabatic expansion, from a pressure of 4550 atmospheres at 40° C. to atmospheric pressure, was 13° C., or 0·00286° per atmosphere, thus agreeing even closely with the preceding estimate.

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Energy Transformations of X-Rays.

By Prof. W. H. Bragg, M.A., F.R.S., and H. L. Porter, B.Sc., Demonstrator of Physics, University of Leeds.

(Received May 15,—Read May 25, 1911.)

The manner of our attack upon the problems of radioactivity, including the action of the Röntgen rays, depends materially on whether we suppose that an atom can or can not be made to yield energy from an internal store. In the former case we have nothing to guide us to an estimate of how much energy may be expected to be put into circulation in this way. If, for example, a β-ray in passing through an atom prompts the atom to emit new secondary radiation with energy drawn from a source usually beyond the reach of transformation into physical or chemical or other known forms, or if the atom sometimes absorbs energy from that of the β-ray motion and locks it up, then the quantities of energy thus added to or subtracted from the amounts we may hope to measure must be no more than subjects of experiment. We shall have to be content with registering them without accounting for them. But if we take the second of the two alternatives the problem is immensely simplified, and we may work for a more complete solution. An α-ray or β-ray begins its career with so much energy. While we cannot, of course, explain this initial liberation of energy, we may try to account completely for its subsequent expenditure in various ways, since we have no unknown or unexpected items to take into account on either side of the balance-sheet.

Exactly the same statement can be made in respect to each X- or γ-ray, since each such ray, as has been shown in previous papers,* can be considered by itself, being independent of all its companions in what we call a "beam of X- or of γ-rays." Energy considerations lead us directly to the supposition that the X- and γ-rays are corpuscular in nature in so far as each ray is a separate identity moving through space unaltered in form and energy-content, just as an unhindered projectile would do. No X- or γ-ray spends energy in its passage through matter; the only way in which the existence of such rays is made manifest is through their replacement by swiftly moving electrons which ionise the gas through which they pass. The single X-ray disappears as such, and in its place is a cathode ray, an electron moving with energy inherited from the X-ray. Ionisation by X- or γ-rays is an indirect process.

* For a summary of the argument, see a paper by Bragg, 'Phil. Mag.,' September, 1910.

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It is not necessarily an exception to this rule that sometimes the absorption of a primary stream of X-rays of definite quality or penetrating power is marked by the appearance of secondary X-rays of different quality. Barkla has shown that many such cases exist, that the secondary rays are characteristic of the substance from which they come, and not of the rays which excite them, and that they can only be excited by rays more penetrating (as measured by absorption in aluminium screens) than themselves. The corpuscular theory leads us to suppose that the more penetrating X-rays as defined in this way are simply those with the most energy. The quality of any X-ray is completely defined by the energy of the cathode particle to which it gives rise. At any rate there seems no ground at present for supposing any other qualification to be required. Barkla's law, then, amounts to this, that many substances under the stimulus of primary X-rays emit secondary X-rays which are characteristic of the substance and not of the stimulating rays, and that a secondary X-ray can only be brought into existence by one having more energy than itself. On the view of the energy question which we are adopting the last assertion in this statement is to be anticipated.

As we have said, this production of secondary X-rays is not necessarily an exception to the rule that absorption of X-rays implies the conversion of their energy into that of cathode rays, and into nothing else. It may well be that the secondary rays are due to a reconversion of the cathode rays into X-ray form, after they have lost energy in moving through the gas in which they arise, or in some other way. Let us, for example, consider the history of a secondary X-ray emitted by zinc under the stimulus of X-rays from a Röntgen bulb. It is an identity of definite energy, and is liable to be replaced in traversing some atom by a cathode ray of definite initial energy; we may speak of the "zinc X-ray" and the "zinc cathode ray." The electron of the zinc cathode ray is not different to other electrons, but it has a definite initial speed and a definite penetrating power. Let us imagine a Zn X-ray penetrating a nickel plate; in some cases the Zn X-ray is replaced by a Ni X-ray, which is an identity of less energy. This change may have taken place in one atom of nickel, which has then absorbed energy equal to the difference between the energies of a Zn X-ray and a Ni X-ray. Or there may be no exception* to the rule that X-rays are replaced by cathode

* In a recent paper Mr. J. Crosby Chapman ('Phil. Mag.,' April, 1911) describes experiments which convince him that this cannot possibly be the process by which the secondary ionisation is excited. Allowing X-rays to fall on bromine vapour he finds that the presence of CO_2 or H_2 makes little difference in the amount of secondary radiation arising in the bromine; whereas, since the CO_2 must get in the way of many

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rays only, and in that case we must suppose an intermediate stage, in which the Zn X-ray has been replaced by a moving electron; in this stage some of the energy is frittered away in ionisation, and only a remainder handed on to the Ni X-ray. We are here supposing that the Zn X-rays are really homogeneous, and consist of a number of "corpuscles" all alike. The homogeneity is taken to be proved by the fact that they are absorbed, according to Barkla, under an exponential law, which naturally implies that, however many rays have been removed from a stream, the remainder possess the same properties. Perhaps there is room to suppose that the quality of Zn X-rays is only an average quality, but it is certainly difficult to understand the exponential absorption in that case.

The foregoing statements are intended to be introductory to the description of certain experimental results. We have attempted to consider and to measure the transformation of X-ray energy in a few cases, since the corpuscular theory would suggest the possibility of success in this direction. If the absorption of X-rays means their conversion into cathode rays, then we ought to find that the production of cathode ray energy is proportional to the disappearance of X-ray energy, at least where there is no production of secondary X-rays. In the latter case we may avoid the uncertainty as to the exact way in which these secondary rays arise, by allowing for the energy contained in them. Whatever energy of the primary rays is then left unaccounted for must be proportional to the cathode ray energy they can produce. Lastly, we can show that X-rays, when they go through a gas, produce enough cathode radiation to cause all the ionisation which is observed, and there is no need to ascribe any direct action to the X-rays themselves.

We take first a pencil of the secondary X-rays from tin, which are relatively energetic, and give rise to penetrating cathode rays. On this account the cathode rays which emerge from a plate on which the Sn

cathode rays and the H_2 cannot do so, the CO_2 ought to interfere with the conversion of cathode rays into X-rays. This does not seem to me conclusive. If the production of X-rays is a consequence of the encounters of cathode rays with bromine atoms there will be ample opportunity for the effect to take place even though the CO_2 molecules are scattered among the Br atoms. If an electron meets a CO_2 molecule first it is not arrested there but deflected, and may have hundreds of encounters still before it: so that its chance of meeting a Br atom is practically as great as ever. If it is argued that the cathode ray is "absorbed" by the bromine and the CO_2 in proportion to weight, it must be answered that whatever "absorption" may mean there is no clear evidence of the universality of Lenard's law. I do not assert that the idea of the intermediate corpuscular stage is established in the simple form in which I have stated it; but it seems to simplify the theory, and is not, I think, disproved by Mr. Chapman's experiment.—W. H. Bragg.

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X-rays fall have a considerable ionising effect, for even those which have their origin in relatively deep layers of the metal can make their way into the open. Our first object is to find the cathode radiation which the Sn X-ray can arouse in different substances, and to compare the various amounts with the absorption coefficients of the substances for those X-rays.

The apparatus is shown in fig. 1. A primary pencil of rays from the bulb passes down a tube lined with tin, and falls upon a plate of tin in a box made of tin. The primary rays fall on nothing but tin, the object being to make the pencil of rays issuing from the box as free as possible from all but Sn X-rays. The secondary rays pass into an ionisation chamber through an

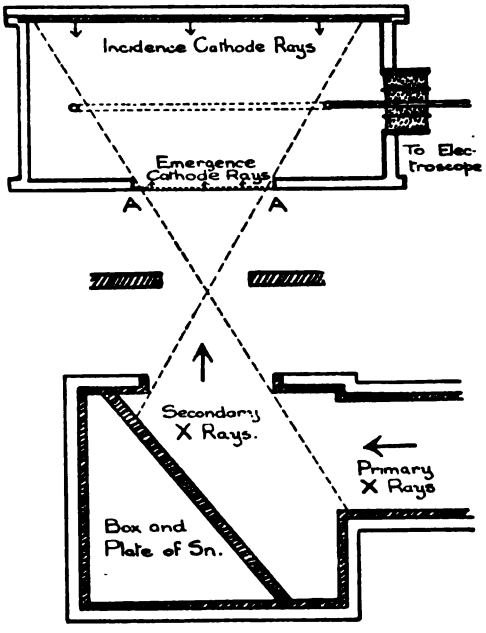

FIG. 1.

opening AA closed with paper. They excite emergence cathode rays in sheets of metal laid on the paper, or incidence cathode rays in plates laid on top of the chamber if such sheets or plates are placed in position. The ionisation current is balanced against a similar current in a second ionisation chamber crossed by a pencil of rays from the same radiator. The second chamber is closed by an adjustable opening worked by a micrometer screw; the values of the readings are determined by a special calibration. A Wilson tilted electroscope is used as a detector. The arrangement works well; consecutive readings rarely differ by as much as 1 per cent. The results of experiment differ by far more than this at different

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times, but it seems as if the bulb were at fault rather than the measuring apparatus.

There are various ways of finding out what fraction of the ionisation current observed is due to the action of the cathode rays at incidence or emergence. It may be done by gradually increasing the depth of the chamber, a method employed by Townsend* long ago. Sadler† has used the same method. Beatty‡ varied the air pressure, which is more convenient in many ways, because it requires no moving parts in the apparatus and makes no change in the geometrical conditions. In some cases it is convenient to increase gradually the thickness of the metal sheet, and to observe the consequent increase in the cathode radiation. Bragg and Madsen§ employed this method when investigating the production of β-rays from γ-rays. It is also very convenient to find the difference between the current when the metal under investigation is bare to the ionisation chamber, and the current when the metal is covered over with a very thin sheet of tissue paper, which cuts off all cathode rays and interferes very little with any others. For this purpose we generally employ carefully flattened plates of metal, one face of each plate being bare and the other covered with tissue paper fixed on with as little adhesive as possible.

In order that results obtained at different times, or with different pieces of apparatus, may be comparable with each other, it is convenient to express each result as the ratio of the ionisation caused by the cathode radiation to the ionisation caused by the X-rays in crossing 1 cm. of air. For example, in one experiment where the plate was made of Sn, with the bare side towards the chamber the current was 247 on an arbitrary scale, and when the plate was turned over so that the tissue paper cut off the cathode rays, the current was 122. Hence the cathode radiation was 125, and, since the chamber was 4·2 cm. across, the ratio required was $125 \times 4{\cdot}2/122 = 4{\cdot}31$. There was no secondary radiation in this case; it is not excited by tin in tin. In the same way we may find the corresponding figure for the "emergence" cathode radiation.

In the case of Ni, Fe, Cu, and Zn, the results are complicated by the presence of the characteristic secondary radiations. The tissue paper no longer cuts off all the radiation from the metal; the cathode rays are absorbed, but the secondary X-rays should be very little affected in passing through the paper. To make sure that this was the true explanation we

* 'Camb. Phil. Soc. Proc.,' 1899, vol. 10, p. 217.
† 'Phil. Mag.,' March, 1910.
‡ 'Camb. Phil. Soc. Proc.,' 1910, vol. 15, p. 416.
§ 'Phil. Mag.,' December, 1908.

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stretched a piece of paper over the top of the ionisation chamber so as to form the upper wall of it. The ionisation current then observed was not increased when plates of tin or aluminium were placed over the chamber on top of the paper, but it was increased when any one of the other metals was placed there. By interposing thin sheets of aluminium or paper between the plate and the paper top to the chamber, it was possible to find an absorption curve. This curve is not exponential; it is of a more complicated form, which we must examine presently when we compare the energy of the secondary radiation with that of the primary.

At this stage it is only necessary to say that when the plate on top was a copper one the curve showed an absorption such as would be expected if the secondary X-rays were Cu X-rays. We may assume, therefore, that we have here an example of the effect described by Barkla, and that the secondary rays excited by the Sn rays are characteristic of the metal in which they arise. The amount of the secondary radiation is conveniently expressed by the ratio of the ionisation it causes in the chamber to the ionisation caused by the primary rays in the same chamber. For example, in an experiment when the rays entered the chamber through a paper screen and fell upon an aluminium plate with the papered face down, the current was 136. When nickel with the papered face down was substituted for the aluminium, the current was increased to 177, and if the nickel plate was turned over so as to present its bare side to the X-rays the current became 296. Thus there was an incidence cathode radiation of 119, and a secondary X-ray effect of 41. The former is recorded as $4{\cdot}2 \times 119/136 = 3{\cdot}67$, and the latter as $41/137$ or $0{\cdot}30$.

The ratio of the emergence to the incidence cathode radiation was determined separately. The following table (p. 355) shows a set of results obtained in this way.

In the case of zinc the ratio of emergence to incidence cathode rays was not actually measured, but assumed to be the same as for copper. The total cathode ray effects and the absorption coefficients clearly run parallel to each other, allowing for the fact that in the case of some of the metals part of the primary X-ray energy is spent in exciting secondary X-rays. But there are several points to be considered before a true comparison can be made.

In the first place the cathode ray effects are caused by such of the cathode radiation as emerges from a plate on which the X-rays fall. This is not exactly what we want; we are trying to compare the cathode radiations excited in equal weights of different metals by Sn X-rays, and we have really no measures of these as yet, for we have not allowed for the

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Table I.—Sn Rays.

I. Radiator.	II. Incidence cathode rays.	III. Emergence ÷ incidence.	IV. Total cathode rays.	V. Secondary X-rays.	VI. k.
Al	0·464	1·80	1·30	0	1·83
Fe	3·59	1·50	9·02	0·184	14·3
Ni	3·67	1·50	9·18	0·301	17·1
Cu	4·11	1·50	10·26	0·301	17·4
Zn	4·29	1·50 ?	10·72	0·308	17·4
Sn	5·20	1·36	12·36	0	12·9

Column I refers to the metal in which the X-rays excite cathode rays.
„ II gives the incidence cathode radiation expressed as already explained.
„ III gives the ratio of emergence to incidence cathode rays.
„ IV gives the total cathode radiation.
„ V gives the secondary X-radiation expressed as already explained.
„ VI gives the absorption coefficient of the Sn rays in each metal.

loss of energy of the cathode rays in their way out of the body of the metals. If the proportionate loss is the same for all metals, it is unnecessary to find it, and there are grounds for believing that in many cases it is. Lenard showed that the cathode rays which he employed were equally absorbed by all substances with atomic weights between those of carbon and gold. The value of the coefficient which he found was 3000 nearly, so that his rays must have been about as penetrating as the Sn cathode rays.* Hydrogen was an exception, having a larger coefficient. Lenard also compared the absorption coefficient of less penetrating cathode rays in some gases, of which the only one with a large atomic weight was argon. Though the coefficient was still much the same in C, O, and N, the H atom had increased its difference. These experiments do not cover the penetration of the slower cathode rays in metals such as Fe, Cu or Zn; and we do not know that the law of equal penetration holds in these cases. They are very difficult to investigate since the absorption coefficients are so high. Confining, however, our attention to the Sn rays for the time being, it seems right to assume Lenard's law to hold to a first approximation. If we do this, the amount of cathode radiation emerging may be taken as a true relative measure of the amount of cathode radiation made.

We must now try to allow for the energy spent in making secondary X-rays. Barkla has shown that such secondary rays are radiated uniformly in all directions about their origin. Let a pencil of rays of energy I enter the upper plate of the ionisation chamber and let k_1 be the absorption coefficient of the plate for these rays. Let k_2 be the absorption coefficient

* Beatty, *loc. cit.*

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for the same plate in regard to its own rays. The loss of energy of the primary in crossing a stratum of weight dx is $k_1 \mathrm{I} e^{-k_1 x} dx$, where x is the mass penetrated previously. Of this the amount that gets back into the chamber is

$$\tfrac{1}{2} \mu k_1 \mathrm{I} e^{-k_1 x} dx \{e^{-k_2 x} + k_2 x \mathrm{Ei}(-k_2 x)\},$$

where μ is the fraction of the primary energy which is directly or indirectly converted into secondary X-ray energy, and the factor in brackets is necessary to allow for the absorption in the stratum of weight x when the rays are distributed uniformly, k_2 having been obtained by measurement with rays normal to the absorbing plate.* The divisor 2 is introduced because half the energy must go each way.

The whole energy of secondary radiation which comes back and crosses the chamber is therefore

$$\tfrac{1}{2} \mu \mathrm{I} \int_0^\infty k_1 e^{-k_1 x} \{e^{-k_2 x} + k_2 x \mathrm{Ei}(-k_2 x)\} dx = \mu \mathrm{I} \int_0^\infty \tfrac{1}{2} \frac{k_1}{k_2} e^{-k_1 y / k_2} \{e^{-y} + y \mathrm{Ei}(-y)\} dy,$$

and is a function, therefore, of k_1/k_2 only.

The value of the integral can be found for a few values of k_1/k_2 by plotting the curve and finding the area. The result is shown in fig. 2, and

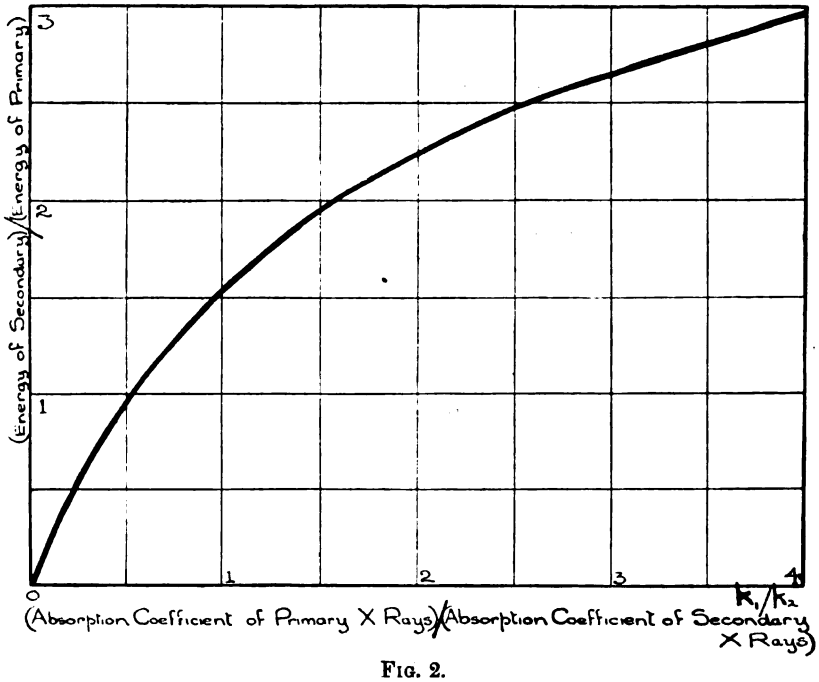

FIG. 2.

* Soddy, 'Phil. Mag.,' May, 1910, p. 735. Values of the constant μ have been already found for a number of cases by Sadler, 'Phil. Mag.,' July, 1909.

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a smooth line drawn through the calculated points gives us the value of the integral sufficiently well for all values of k_1/k_2.

In the case for example of Sn rays incident on Cu, since $k_1 = 14{\cdot}5$ and $k_2 = 53$ so that $k_1/k_2 = 0{\cdot}274$, the value of the integral is found from the curve to be 0·0588; or

$$\frac{\text{Energy of secondary crossing the chamber}}{\text{Energy of primary crossing the chamber}} = \mu \times 0{\cdot}0588.$$

Now the absorption coefficient of Sn rays in C is 0·32 nearly, and of Cu rays in C is 5·22, and the ratio of the coefficients in air will be the same practically as in C. Also the ionisation of the air is proportional to the absorption coefficient of the air; hence

$$\frac{\text{Ionisation in chamber due to secondary rays}}{\text{Ionisation in chamber due to primary rays}} = \mu \times 0{\cdot}0588 \times 5{\cdot}22/0{\cdot}32 = \mu \times 0{\cdot}96.$$

By actual experiment the ratio of these ionisations is found to be 0·301, and therefore $\mu = 0{\cdot}313$. That is to say, 0·313 of the absorbed energy of the primary is spent in producing secondary Cu rays, and only 0·687 of the energy remains to be accounted for in cathode ray energy. There is still one correction to be made, which is only of importance, however, in the case of aluminium. When we measure cathode rays in this way we measure actually the difference between the cathode radiation from the metal in question and the cathode radiation from the tissue paper with which we have covered one face of it. The results we obtain are therefore comparable with the difference between the absorption coefficients of the metal and the paper. In the case of Sn rays the absorption coefficient of carbon is about 0·32. Making all these allowances we obtain a set of results which are set out in Table II.

On the whole the figures in the last column agree very well, quite as closely as we can expect considering the sources of uncertainty which we have pointed out. So far, therefore, we may conclude that the relationship between the cathode radiation and the absorption coefficient is as it should be.

Experiments with arsenic X-rays gave the results set out below in Table III. Only the incidence cathode rays were taken into account, for the measurement of emergence cathode rays is unsatisfactory unless the plate through which the X-rays enter the chamber is very thin indeed. The thinnest sheets obtainable of most substances were sufficient to harden the X-rays a little in spite of their approximate homogeneity, and there was a certain small fraction of scattered primary X-radiation included in the secondary radiation from the arsenic. A very little penetrating radiation in

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Table II.—Sn Rays.

I. Radiator.	II. Cathode rays.	III. Secondary X-rays.	IV. μ.	V. k.	VI. $k(1-\mu)$.	VII. $k(1-\mu)-0{\cdot}32$.	VIII. VII/II.
Al	1·30	0	0	1·83	1·83	1·51	1·16
Fe	9·02	0·184	0·155	14·3	12·1	11·8	1·30
Ni	9·18	0·301	0·262	17·1	12·6	12·3	1·34
Cu	10·26	0·301	0·313	17·4	11·9	11·6	1·13
Zn	10·72	0·308	0·356	17·4	11·2	10·9	1·02
Sn	12·36	0	0	12·9	12·9	12·6	1·02

Column I. Name of metal in which the cathode and secondary X-rays are excited.
„ II. Amount of cathode radiation measured as described above.
„ III. Amount of secondary X-radiation.
„ IV. Calculated value of ratio of secondary to primary X-ray energy.
„ V. Absorption coefficient of primary X rays by the metal.
„ VI. Proportion of the absorption which should go to the production of cathode rays.
„ VII. The same, less the absorption coefficient of paper (see above).
„ VIII. Ratio of VII to II.

a fairly homogeneous beam produces a material alteration in the cathode radiation. For example, Beatty's figures on p. 324 of the paper already quoted and published in the 'Phil. Mag.,' August, 1910, show that a stream of Sn X-rays producing the same effect in air as a stream of As X-rays produces seven times as much cathode radiation in silver.

As it happens, there is very little difference between the emergence and incidence cathode rays in such cases as we have examined, and it seems justifiable therefore to work with the incidence rays only.

The arsenic radiator was made of the same form as the tin radiator; tube, box, plate and all parts on which the primary rays could fall were made of thick card on which metallic arsenic in a powdered form had been fastened by a little gum. Perhaps the gum scattered a little hard primary radiation, for our absorption coefficients were somewhat smaller than those of Barkla and Sadler.

We know hardly anything of the absorption coefficients of As cathode rays. Assuming that they also follow Lenard's law, the figures in the last column should be all the same. They are so approximately. Some results obtained with Zn rays may be given. As with arsenic rays, they are difficult to interpret fully until more is known of the absorption of the special cathode rays in different metals. There is also more liability to experimental error since the cathode radiations are so small in many cases. We have, therefore, following Beatty's plan, worked at low pressures so as to make the cathode ray effect greater relative to the effect of the X-rays. Even then it is difficult to find accurate results, for when zinc rays fall on a metal such as aluminium

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Table III.—As Rays.

I. Radiator.	II. Incidence cathode rays.	III. Secondary X-rays.	IV. μ.	V. k.	VI. $k(1-\mu)$.	VII. $k(1-\mu)-2\cdot5$.	VIII. VII/II.
Al	0·115	0	0	23·6	23·6	21·1	183
Fe	0·420	0·187	0·200	127	101·6	99·1	235
Ni	0·500	0·165	0·293	147	106	103·5	207
Cu	0·483	0·217	0·340	155	102	99·5	206
Zn	0·536	0·190	0·371	186	117	114·5	213
Sn	0·575	0	0	112	112	109·5	191

For description, see notes to Table II.

the cathode ray effect is only 10 per cent. of the whole at a pressure of 8 cm. of mercury, the chamber we employed being 3·45 cm. deep. The curves in fig. 3 give a general idea of the relative magnitude; for each metal the firm line shows the variation of ionisation with pressure of air when the metal is

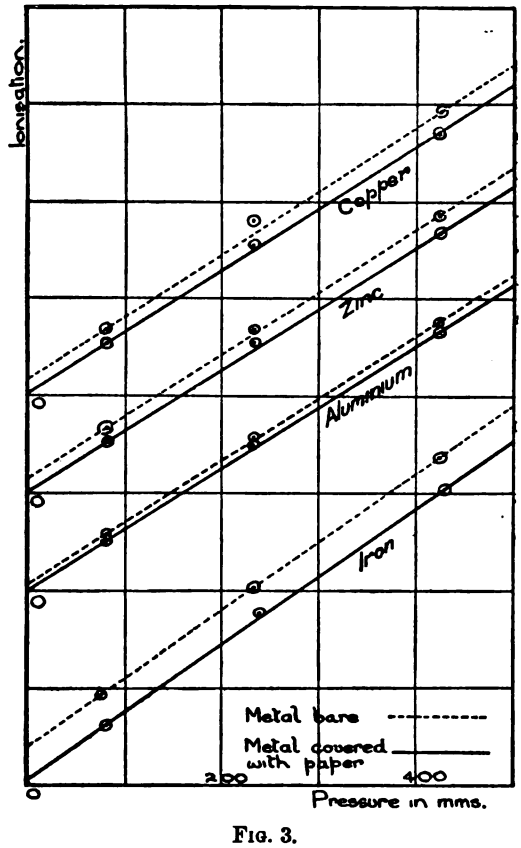

Fig. 3.

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covered with tissue paper and the broken one shows the effect when the metal is bare. The lines are drawn straight though clearly they should all be slightly curved in order to fit the points; the figure seems easier to examine with the lines drawn as they are.

The results are collected in the following table:—

Table IV.—Zn Rays.

I. Radiator.	II. Incidence cathode rays.	III. Incidence secondary X-rays.	IV. μ.	V. k.	VI. $k(1-\mu)$.	VII. $k(1-\mu)-4\cdot5$.	VIII. VII/II.
Al	0·060	0	0	39	39	34·5	575
Fe	0·33	0·135	0·204	221	176	173·5	525
Ni	0·39	0·132	0·274	265	192	187·5	480
Cu	0·21	0	0	55	55	50·5	240
Zn	0·11	0	0	50	50	45·5	415
Sn	0·38	0	0	225	225	220·5	580

For description, see notes to Table II.

The parallelism between the absorption coefficients and the production of secondary radiations is quite clear; and when due allowance is made for the energy which reappears as secondary X-rays, there is a fair agreement between the production of cathode rays and the energy which presumably goes to make them. Copper does not agree with the others; and we have no reason to give as yet for the divergence. It is to be remembered that agreement cannot be expected unless Zn cathode rays are equally absorbed in all substances, and we have no sure knowledge that they are.

Beatty* has traversed the field in a cross direction. He has allowed X-rays of various types, viz., those from Fe, Cu, Zn, As, and Sn to pass through a silver leaf, and has measured the "emergence" cathode radiation arising from the silver in each case, expressing the result as a ratio of the ionisation caused by it to the ionisation caused by the X-rays in a layer of air 1 cm. thick immediately after passing through the silver. It is necessary, of course, to use some such standard of reference. The ratio is called C in Table I of his paper (p. 324). He also measured the absorption coefficient (λ) of the cathode rays in air by finding the thickness of air stratum required to reduce the cathode radiation to half value (t in the same table) and dividing this into 0·7. This process depends on the assumption of an experimental law of absorption. The absorption does not really fulfil this law, as his own diagrams show; but for the purpose of argument it was no doubt justifiable to make

* 'Phil. Mag.,' August, 1910.

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the assumption for the sake of convenient expression, and he was concerned only with the relative amounts of the cathode radiations produced in silver by the different rays. If the assumption of the exponential law made an error in one case, it probably made the same error in the others.

He then assumes, further, that the λ in silver is proportional to the λ in air for all these types of X-rays, so that while C is a measure of the emergence cathode radiation only, $C\lambda$ is a measure of all the cathode radiation that is produced, not merely of what gets out of the silver. It is the ratio of the ionisation due to this radiation (if it could all get out) to the ionisation due to the X-rays in 1 cm. of air.

He assumes, still further, that the ionisation of the air by the X-rays is proportional to the absorption of those rays by the air; and, again, that the absorption of X-rays by the air is proportional to their absorption by silver. The constancy of the quantity $C\lambda$ therefore enables him to draw his final conclusion that, "in the case investigated, a constant fraction of the homogeneous radiation is spent in producing cathode particles."

Some of Beatty's assumptions are certainly justifiable, the third, at any rate, and probably the fourth; the first is permissible for the occasion, and the second may very well be true, but there is no definite proof of it.

The corpuscular theory would lead us to anticipate Beatty's result: it would, indeed, go further still, and assert that the constant fraction is unity, at least in the case where there is no secondary X-radiation in addition to the cathode radiation. There was none in Beatty's experiment. If we aim at an experimental verification of this simpler but more comprehensive deduction from the corpuscular theory we cannot assume an exponential law for the absorption of the cathode rays in the silver. We must make some attempt to find the true law.

We pass Sn rays into an ionisation chamber through an opening closed by a card. The whole of the chamber, which is made of brass, is lined with Al and paper, so that there is no radiation from the walls to be taken into account. Silver foils are then laid on the card, and the increase in ionisation is observed as the number of foils is increased. The curve obtained is shown in fig. 4. If we can find the slope of this curve at the origin we shall know the cathode radiation for extremely thin sheets, which is what we really require; for if the sheets were very thin all the cathode rays would get out. Unfortunately silver foil is not to be had thin enough to give any points nearer the origin than are shown in the figure, and we are left to draw the curve through the experimental points as we think it ought to be drawn. Beatty assumed the exponential curve passing through the point for which the current measured is half the final value. This is represented by the

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dotted line in the figure, and OQ is the tangent at the origin. The true curve would seem to be somewhat different and less steep initially. The simplest form to assume is parabolic, viz., $y = ax - bx^2$, and such a curve has been drawn so as to pass through the origin and the first two points; it then

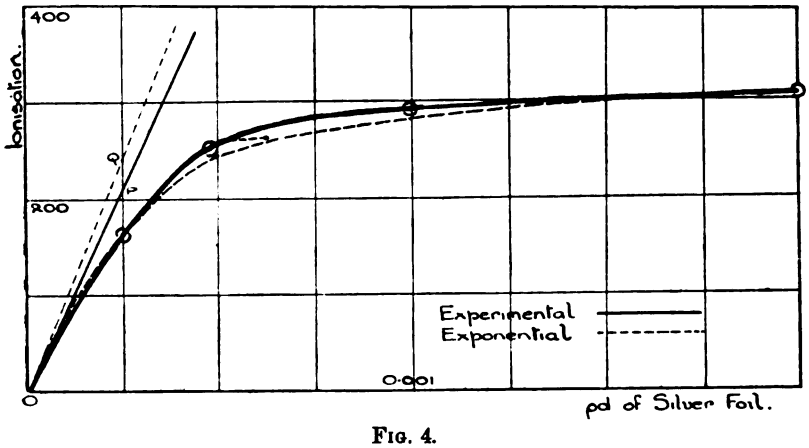

FIG. 4.

breaks away as shown. Adopting this form, it is easy to find the tangent at the origin, OP; and it appears that initially emergence cathode rays are produced and make their way into the open at the rate of 208 to a weight of screen of 0·00025 gr./cm.^{2}. The maximum reading due to cathode rays is 309. We derive from this curve the fact that when the maximum emergence radiation is 309, the actual production of emergence cathode rays is 4×208 or 832 per milligramme of silver. The ratio of these two numbers, $832/309 = 2{\cdot}69$, and is all that is required for future calculation. If we had assumed an exponential curve passing through the point on a curve at which the ordinate is half its greatest height we find that the tangent at the origin, OQ, gives a value for this ratio about 15 per cent. higher.

In order to find the full amount of the cathode radiation produced in silver we must also take into account that which would be found on the incidence side of a very thin sheet. We must do the same thing in regard to incidence cathode rays as we have just done in regard to emergence. This might be done by gradually thickening a silver sheet on top of the chamber on which the X-rays fall: but there is always some uncertainty about this method, since some of the X-rays which enter the chamber might —through scattering or otherwise—strike the walls rather than the top plate. When dealing with the emergence cathode radiation no such thing can happen. It is perhaps simpler to compare the incidence and emergence cathode rays by laying one or more silver foils on a card and placing this in

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the middle of the ionisation chamber, so that the X-rays must go through it. The cathode radiations are then found by subtracting the current for a bare card from the current when there are silver foils on one side or the other. We found the ratio between incidence and emergence to be 1·30 for one, two, or three foils; and we conclude that this ratio may be supposed to hold for extremely thin films. The distribution of the cathode rays about the silver atom is therefore unsymmetrical from the first, though it is by no means so uni-directional as in the case of the β-rays caused by γ-rays.

The measurements made so far were obtained in air, because it was convenient to adjust the silver foils in a chamber which could be easily opened and closed. But the remaining part of the experiment was carried out with oxygen instead of air, since it was necessary to compare the absorption coefficient of the Sn rays in the silver and in the gas employed. It is difficult to measure accurately the absorption of Sn rays in a gas since it is so very small, and air can only be used as gas. But the absorption in oxygen can be found by using solid absorbing screens containing known quantities of oxygen. This part of the experiment will be described presently.

It was now necessary to find the ratio of the emergence radiation from the silver, measured by the ionisation it causes in oxygen to the ionisation in a given layer of oxygen due to the Sn X-rays. Employing the same method as Beatty, we passed Sn rays into an ionisation chamber which could be filled with gas at any pressure. The rays passed in through ten silver foils, which were amply sufficient to give the full cathode radiation. The depth of the chamber was 3·45 cm. The curve obtained is given in fig. 5, and gives us

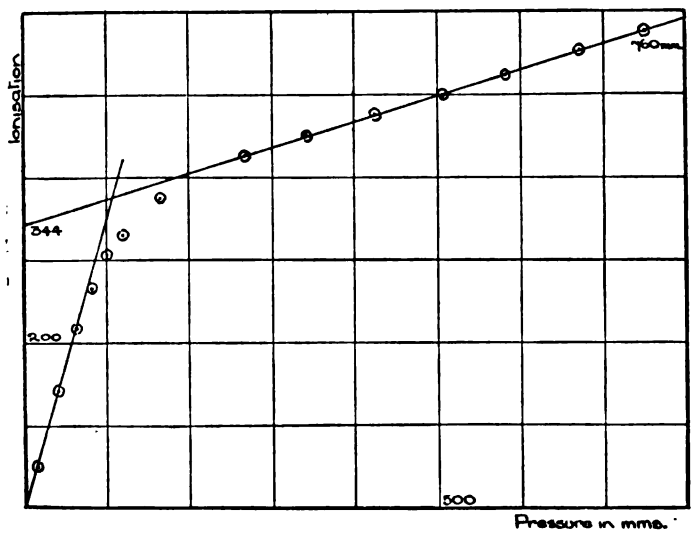

FIG. 5.

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the means of calculating the ratio we require. The ionisation due to the emergence cathode rays is 344, while that due to the X-rays crossing 3·45 cm. of oxygen at 76 cm. pressure is 227. Hence the ratio of the effect of the emergence cathode radiation to the effect of the X-rays crossing 1 milligramme of oxygen is

$$344 \times 3{\cdot}45 \times 1{\cdot}37/227 = 7{\cdot}16,$$

the density of oxygen being 0·00137.

We have already found that the cathode radiation per milligramme of silver is 2·69 times the emergence cathode radiation from silver, a result which was found by the use of air, but must be just the same when oxygen is used. Combining these figures with the ratio of the whole cathode radiation to the emergence radiation (viz., 2·3/1·3) we have finally that in equal weights of silver and oxygen there is $7{\cdot}16 \times 2{\cdot}69 \times 2{\cdot}3/1{\cdot}3 = 34$ times as much* ionising power in the cathode rays produced by the X-rays in the silver as there is ionisation actually effected by the X-rays going through the oxygen.

We next require the ratio of the absorptions of the Sn rays in silver and in oxygen. Using the same apparatus and keeping all the conditions the same in the absorption experiment as in those that went before, we found the absorption coefficient of the X-rays by the silver to be 15·4. The very soft portion of the Sn rays was intercepted by a wooden plate which closed the ionisation chamber, and was used throughout because it stood air pressure without cutting out many Sn rays. The absorption coefficient of C was found to be 0·333 and of oxalic acid to be 0·388. From Beatty's results the absorption coefficient of H is negligible. Hence we can calculate the absorption coefficient of oxygen from the equation

$$12 \times 0{\cdot}333 + 48x + 3 \times 0 = 63 \times 0{\cdot}388,\dagger \text{ and therefore } x = 0{\cdot}425.$$

Consequently silver absorbs Sn rays 15·4/0·425, or 36·3 times as much as oxygen. From the earlier results in this paper we therefore conclude that Sn rays produce 36·3 times as many cathode rays in silver as in oxygen, so that the ionising power of the cathode rays produced by the Sn X-rays in 1 milligramme of silver is 36·3 times the ionising power of the cathode rays produced by the same X-rays in 1 milligramme of oxygen. Comparing this with the result of the last paragraph we see that the ionisation effected in

* That is to say, the total ionisation they would cause in oxygen if they could all complete their whole courses in the gas.

† For, allowing for water of crystallization, there is one carbon atom to three of oxygen and three of hydrogen.

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the same way by the X-rays in crossing oxygen is really effected indirectly through the cathode rays. This confirms the deduction from the corpuscular theory of X-rays that there is here no ionisation by the direct action of the X-rays themselves.

Summary.

The corpuscular theory of X-rays leads us to suppose that the production of cathode rays should follow from the disappearance of X-rays of like energy, and that the former should alone be the cause of ionisation. When Sn X-rays are allowed to fall on different substances the quantities of cathode radiation emerging from the substances are easily measured; from these it is possible to estimate the amount of cathode radiation actually produced in a given weight of metal through the absorption of a given quantity of X-radiation. The difficulties met with and the approximations made in finding the estimate are discussed, and, in particular, the lack of accurate information on the absorption of cathode rays of various speeds. The amounts of cathode radiation produced are then compared with the absorption coefficient of the Sn rays.

The results obtained support the first deduction mentioned above. It is possible therefore to assume that Sn X-rays produce equal cathode radiations in oxygen and in silver for equal expenditures of energy, and it is then shown that when X-rays pass through oxygen the cathode radiations in the gas are sufficient to account for all the observed ionisation, so that there is nothing left for the X-rays to do. This agrees with the second deduction.

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The Mechanical Viscosity of Fluids.

By T. E. STANTON, D.Sc., M.Inst.C.E.

(Communicated by R. T. Glazebrook, F.R.S. Received May 16,—Read June 29, 1911.)

(From the National Physical Laboratory.)

The experiments described in the following paper were undertaken in order to investigate the relation between shearing stress and rate of distortion in fluids which are in eddying or sinuous motion, that is, motion in which the frictional resistance, at the boundaries of the solid over which they move, varies approximately as the square of the relative velocity, as distinguished from that steady or laminar motion in which the frictional resistance is proportional to the first power of the relative speed.

This shearing stress has been called by Osborne Reynolds* "mechanical viscosity," *i.e.*, a "viscosity arising from the molar motion of the fluid and which is not a property of the fluid independent of its motion as is its physical viscosity." Thus, to quote Reynolds' statement, in the eddying motion of a fluid in a parallel channel, "although the mean motion at any point taken over a sufficient time is parallel to the axis of the pipe, it is made up of a succession of motions crossing the pipe in different directions." In this case, the shearing stress at this point on a cylindrical surface coaxial with the pipe "will include the momentum per second parallel to the pipe carried by the cross streams across the surface on which this shearing stress is measured." On the other hand, "the coefficient of physical viscosity is the coefficient of instantaneous resistance to distortion at a point moving with the fluid."

As far as the author is aware, no attempts have yet been made to measure the shearing stress in fluids which are in eddying motion, but Osborne Reynolds has assumed that this stress is proportional to the mean speed of flow, and is also a function of the dimensions of the channel in which the motion takes place.

For experimental purposes, it appeared obvious that the conditions under which the phenomenon could be most conveniently studied were those of the motion of air or water in parallel pipes of circular cross section, and as all the appliances used for the determination of the friction of air in pipes at the National Physical Laboratory were available, air was the fluid chosen for the

* "Theory of Lubrication," 'Phil. Trans.,' 1886, p. 165.

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experiments. Another reason for the choice of air was that in Threlfall's* observations on the distribution of mean axial velocity in air flowing through large pipes this distribution at any cross section appeared to be independent of the rate of flow. Further, although in Threlfall's experiments the general form of the velocity curve does not appear to have been investigated, yet the observed values of the radial gradient of velocity gave some hope of the possibility of an accurate determination of the rate of distortion. If this was found to be the case, a further determination of the variation of pressure along and across the pipe would furnish the data necessary for the estimation of the ratio of the shearing stress to the rate of distortion.

Thus, if F is the average shearing stress on the surface of any cylindrical portion of radius r of the fluid coaxial with the pipe through which it flows, and v the mean axial velocity of the fluid at this radius; then, writing $F = \mu' dv/dr$, the object of the experiments was the determination of μ', which may be called the coefficient of mechanical viscosity, as a function of v and the dimensions of the pipe.

The Method of Establishing the Air Current and Estimating the Values of F *and* v.

The arrangement of one of the experimental pipes and the air fan used to set up the current is shown in fig. I. The air fan discharges into a horizontal pipe 3·5 metres in length. This pipe is connected by a bend to a vertical pipe 5·5 metres high. The experimental portion, 61 cm. long, is at the upper extremity of the vertical pipe. It was found by experiment that this length of outlet was sufficient to set up the limiting distribution of the velocity across the pipe as long as the diameter did not exceed 7·5 cm. The fan was driven by an electric motor, which was provided with a sensitive speed indicator, and during the observations at any given speed of flow the speed of the motor was kept constant by hand regulation of a carbon resistance in the armature circuit of the motor.

The values of v were determined from the difference between the pressure in a small Pitot tube facing the current and that in a small orifice in the side of the pipe. The Pitot tube was of rectangular section, the dimensions at the orifice being:—

In the direction of the radius of the pipe	External,	0·33 mm.
	Internal,	0·25 „
Perpendicular to the radius of the pipe.....	External,	1·27 mm.
	Internal,	1·20 „

* "Motion of Gases in Pipes," 'Inst. Mech. Engineers Proc.,' 1904.

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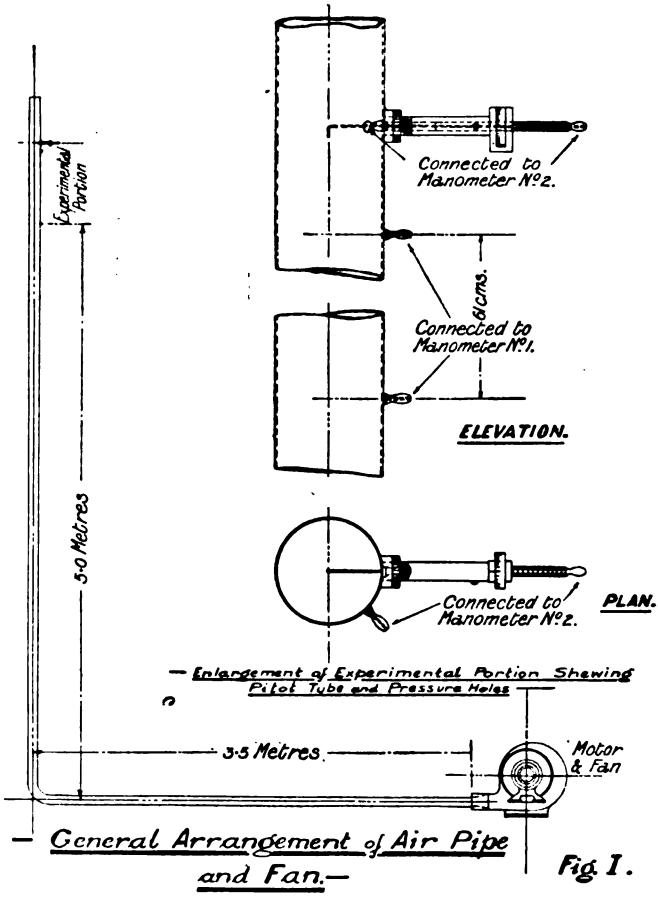
This tube was fixed to a micrometer, and could be moved across a diameter of the pipe. The pressure difference was measured by a sensitive oil-and-water tilting gauge, whose indications could be relied upon within an accuracy of 0·005 mm. of water. The final calibration of the Pitot tube was made by a comparison of its readings with the measured discharge of the pipe through a gas meter.

The determination of the shearing stress on any cylindrical portion of the



General Arrangement of Air Pipe and Fan.

Fig I.

fluid of radius r was made by a direct measurement of the drop of pressure at the surface along the pipe, together with the measurement of the variation of pressure along the radius. The former was observed by taking the pressure difference in two small tubes let into the sides of the pipe. As regards the latter, it has been shown by Osborne Reynolds* that although in steady motion $dp/dr = 0$, when the motion is sinuous $d/dr \cdot (p + \rho w^2) = 0$, where w

* 'Nature,' 1898, p. 468.

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is the component of sinuous motion normal to the surface. To detect such a variation, a small tube of radius 0·4 mm., with a hole in its side connected to a sensitive gauge, was moved across a diameter, but no variation of pressure could be found up to a distance of 2·0 mm. from the walls. It was therefore assumed in the reductions that the pressure was constant across any section, and that the shearing stress was, therefore, proportional to the radius.

(A) Experiments on Artificially Roughened Pipes.

As in ordinary smooth pipes it is known that the frictional resistance varies as a lower power of the velocity than the square, and that in consequence, as shown by Lord Rayleigh,* the friction is given by

$$F = \rho v_c^2 f(\nu/v_c l),$$

where ν = kinematical coefficient of viscosity, l = the linear dimension of the pipe, and v_c the velocity at the axis of the pipe.

In order to simplify the problem, an attempt was made to eliminate any effect due to a variation in $f(\nu/v_c l)$ by artificially roughening the pipes used until the friction was proportional to the square of the velocity. This was done by cutting a double screw-thread on the inside surface of the pipes, and so varying the pitch and depth that the surfaces of pipes of different diameters were geometrically similar.

After several trials, two pipes were produced, of diameters 7·35 and 5·08 cm., in which the friction varied as the square of the velocity, and consequently the friction per unit area at the same velocities was found to be the same for each pipe, the numerical value being $4{\cdot}6\ v_c^2 \times 10^{-6}$ dynes per square centimetre. The results of a large number of experiments on these two pipes were as follows:—

Effect of Velocity of Flow on the Radial Distribution of Velocity.

To test the constancy of the velocity distribution in a radial direction, two sets of observations were made at the highest and lowest centre filament velocities which could be satisfactorily obtained. These were 2220 and 546 cm. per second respectively. The two sets of reduced velocities for the 7·35 cm. diameter pipe are plotted in fig. II, and it will be seen that for this range of speed there is no definite change in the form of the curve, which, from the centre up to a distance of about 3 mm. from the wall of the pipe, is a parabola with its vertex in the axis of the pipe, the equation to which may be written

$$v = v_c - Ar^2.$$

* 'Report of Advisory Committee for Aeronautics,' 1909–10, p. 38; also 'Phil. Mag.,' 1892, p. 59.

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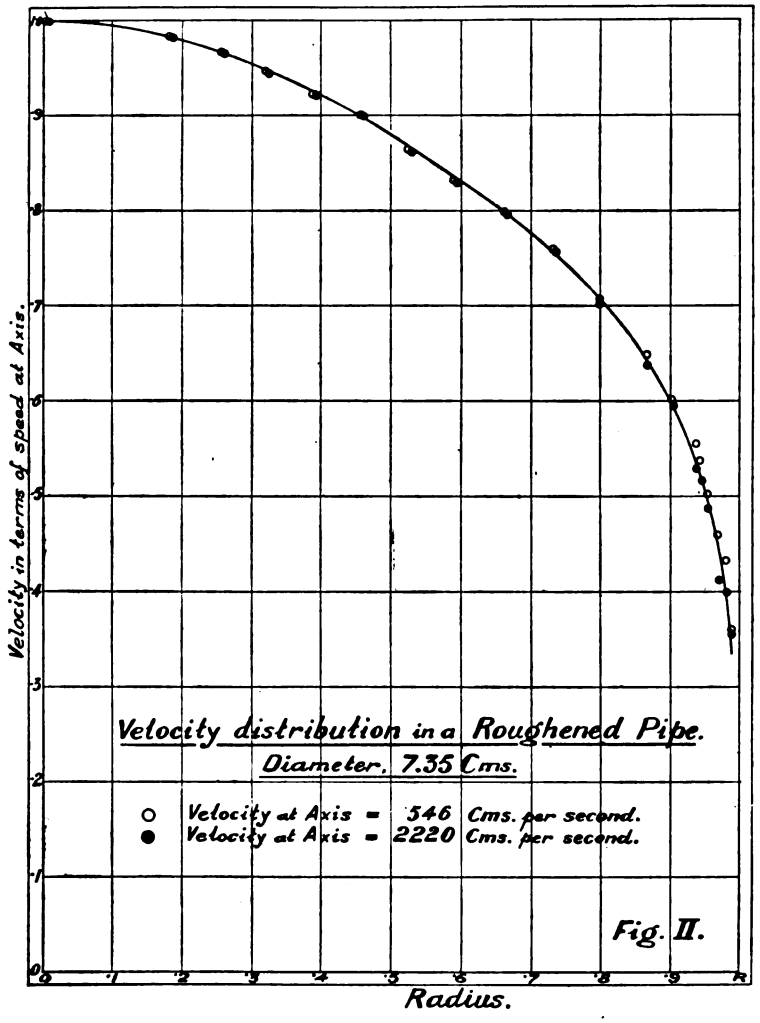
Velocity in terms of speed at Axis.
Velocity distribution in a Roughened Pipe.
Diameter, 7.35 Cms.
Velocity at Axis = 546 Cms. per second.
Velocity at Axis = 2220 Cms. per second.
Fig. II.
Radius.

From the constancy of the form of the curve, A is proportional to v_c, so that for any fixed value of the radius the value of dv/dr, which varies as A, is proportional to v_c. The plotted values of the velocities at points on the radius nearer than 3 mm. from the wall are found to be appreciably below the parabolic curve through the inner values, which apparently indicates that the screw-cutting of the surface has not entirely broken up the region of viscous flow at the boundary.

Effect of Radius of Pipe on the Distribution of Velocity.

As regards the effect of the diameter of the pipe on the velocity distribution, it was found that if in the two pipes the velocities at the axes

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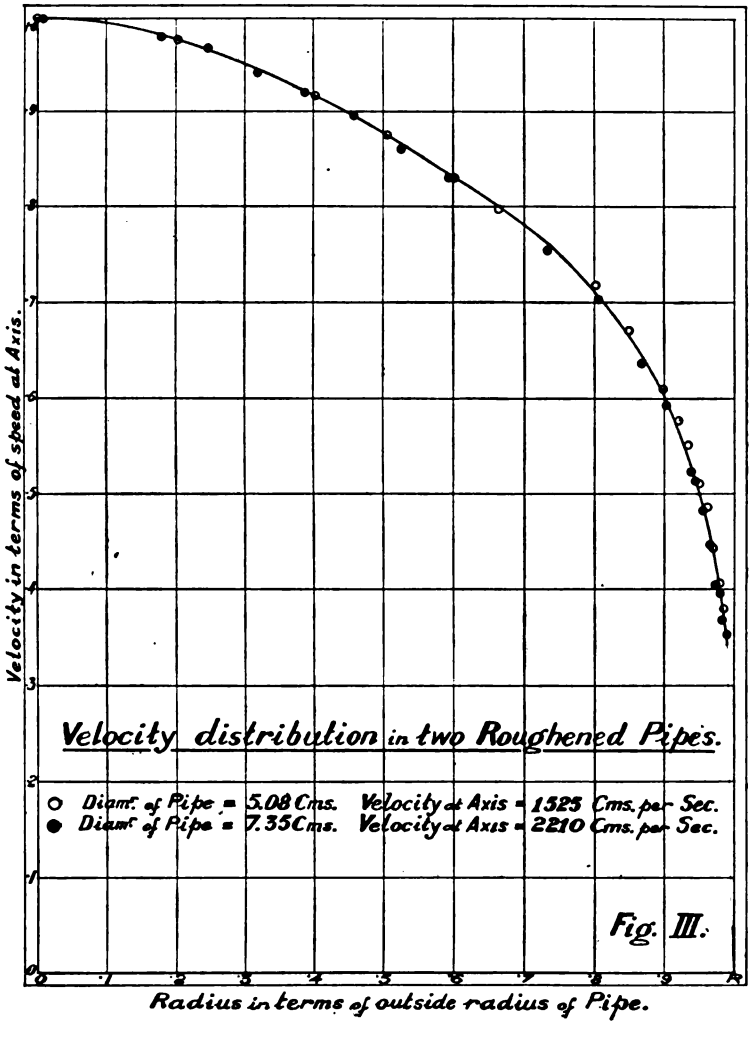
were made proportional to the corresponding diameters, the two velocity curves thus determined were precisely similar, so that for corresponding points on the radii the values of dv/dr were the same for each pipe.

This result is shown in fig. III, in which the velocity curve for the 7·35 cm. pipe, with a velocity at the axis of 2210 cm. per second, is plotted to scale


Velocity in terms of speed at Axis.
Velocity distribution in two Roughened Pipes.
○ Diam.r of Pipe = 5.08 Cms. Velocity at Axis = 1525 Cms. per Sec.
● Diam.r of Pipe = 7.35 Cms. Velocity at Axis = 2210 Cms. per Sec.
Fig. III.
Radius in terms of outside radius of Pipe.

and the corresponding curve for the 5·08 cm. pipe, with a velocity at the axis of 1525 cm. per second, is plotted with the abscissæ and ordinates strained in the ratio of the diameters, *i.e.*, 1·45. It is evident from the coincidence of the two curves that the condition of similarity is fulfilled. The actual values of the velocities are also tabulated in Table I.

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Table I.—Reduced Values of the Velocities in the two Roughened Pipes (v_c/l constant).

Diameter 5·08 cm.		Diameter 7·35 cm.	
Radius.	Velocity in cm. per sec.	Radius.	Velocity in cm. per sec.
0	1526	0	2210
0·52	1495	0·661	2172
0·77	1450	0·917	2132
1·02	1404	1·17	2081
1·28	1342	1·42	2038
1·53	1278	1·68	1986
1·785	1200	1·92	1914
2·04	1092	2·18	1842
2·165	1023	2·44	1762
2·29	937	2·71	1674
2·345	887	2·95	1553
2·380	845	3·20	1400
2·42	785	3·33	1311
2·445	758	3·46	1162
2·470	688	3·485	1137
2·495	628	3·52	1074
2·51	585	3·56	1000
		3·58	946
		3·61	887
		3·635	811
		3·65	780

From the foregoing results the following conclusions for these roughened pipes are derived:—

(*a*) In such a pipe, through which air is moving at a speed above the critical value, it follows from the parabolic form of the curve that the mechanical viscosity, as defined above, is constant across the pipe* up to within a relatively small distance from the boundary.

(*b*) Considering the variations in the shearing force on any cylindrical surface coaxial with the pipe due to variations in the velocity of flow, it is evident that, since the value of dv/dr is proportional to v_c, the velocity of the centre filament, and the shearing force varies as the square of the velocity, therefore μ' is directly proportional to the velocity of flow.

(*c*) In two pipes in which the velocities of flow are made proportional to the diameters the values of dv/dr on two cylindrical surfaces, one in each pipe, whose linear dimensions are proportional to these diameters, are the same. It follows, therefore, that, since the respective shearing forces vary as the squares of the corresponding velocities of flow, the values of μ' must, for different pipes, be directly proportional to the diameters.

* The equation to the velocity curve being $v = v_c - Ar^2$, $dv/dr = -2Ar$; and since F is known to be proportional to r, it follows that μ' in the relation $F = \mu' dv/dr$ is constant.

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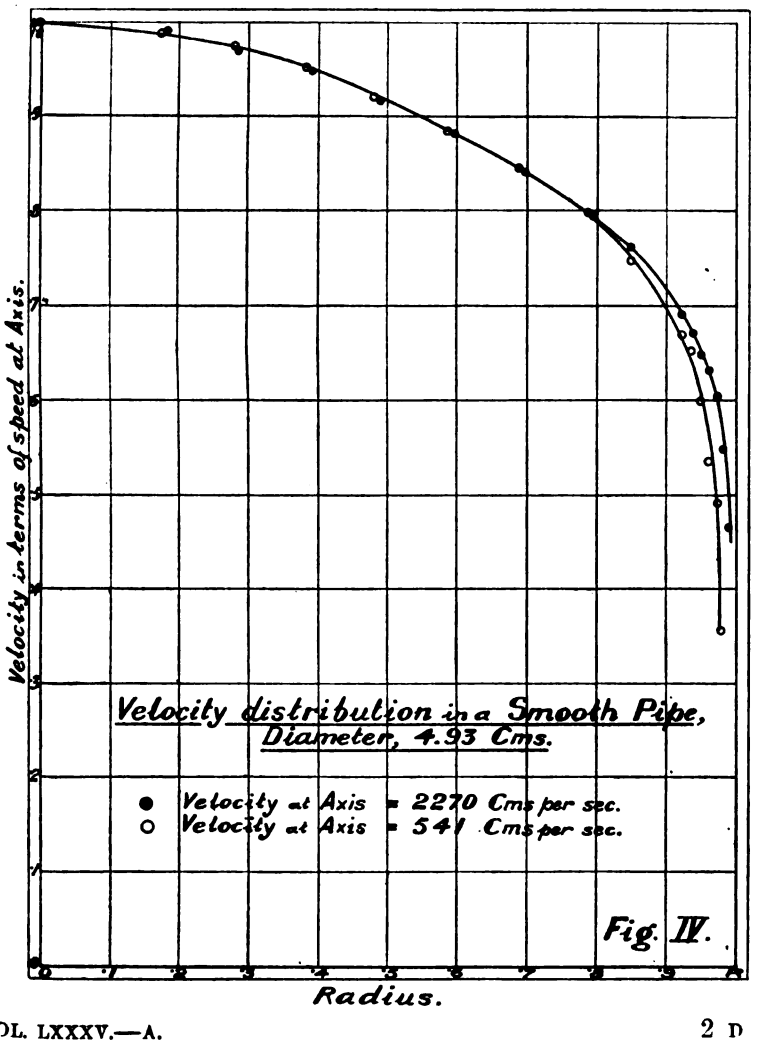
It appears, therefore, that the expression for the coefficient of mechanical viscosity in the artificially roughened pipes considered may be written

$$\mu' = k v_c l,$$

where v_c is the velocity of flow at the axis of the pipe, l the linear dimension of the pipe, and k is a constant depending on the extent of the eddying motion, *i.e.*, the roughness of the surface.

(B) Experiments on ordinary Smooth Pipes.

For these experiments two smooth brass pipes of approximately the same diameters as the artificially roughened ones were used. (These were 4·93 and 7·4 cm. diameter.) As in the case of the rough pipes, two sets of observations,


Velocity in terms of speed at Axis.
Velocity distribution in a Smooth Pipe, Diameter, 4.93 Cms.
● Velocity at Axis = 2270 Cms per sec.
○ Velocity at Axis = 541 Cms per sec.
Fig. IV.
Radius.

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one at the highest speed of flow obtainable and the other at the lowest, were made on one of the pipes, and the distributions of axial velocity in the two cases are shown in fig. IV. It will be seen that, for a region extending from the axis up to a value of the radius of approximately 0·8 R, the distributions are identical, but that beyond this radius the curves separate, indicating apparently a region of viscous flow near the walls, in which the slope of the velocity curves necessarily increases at a greater rate than the centre filament velocity, since the resistance varies as a power of the speed greater than unity. It may be mentioned that in the earlier experiments the corresponding curves plotted from the observations were not anywhere coincident, except at the axis, but, as a possible explanation of this was the insufficient length of the pipe between the fan and the portion under observation, further experiments were made with an increased length of pipe, and it was ultimately found that with a total length of 9 metres there was practical coincidence within the region mentioned. It is of course possible that even then the coincidence was not exact, but the difference, if any, was too small to be detected by the gauges. It was evident, therefore, that in the case of smooth pipes the region of viscous flow was of considerably greater area than in the case of the roughened pipes, in which it appeared to be nearly destroyed. It was, however, found that the central portion of the velocity distribution curve in the smooth pipes up to a radius of 0·8 R was parabolic in form, as in the case of the roughened pipes, thus indicating that the value of μ' was constant up to this limit.

As regards the effect of the size of the pipe, a precisely similar investigation to that used for the roughened pipes showed that, for two pipes in which the centre filament velocities were proportional to the respective diameters, the velocity distributions were strictly similar throughout the central portion of the flow referred to above.*

Considering, therefore, this region, since the values of dv/dr for any given value of the radius are proportional to the velocity of flow, and since the friction per unit area at this radius is known to be proportional to $\rho v_c^2 f(\nu/v_c l)$, it is evident that in the case of the smooth pipe μ' is proportional to $v_c f(\nu/v_c l)$. Further, since for two smooth pipes in which the centre filament velocities are proportional to the respective diameters the values of dv/dr at corresponding points in the central region are the same, it follows that μ' is also proportional to the external diameter of the pipe, and the

* The two velocity curves for this case have not been plotted as in the case of the rough pipes (fig. III), because the difference in the radii is too small to bring out their divergence in the region of viscous flow. The values of the velocities determined are given in Table II.

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complete expression for the mechanical viscosity for the region in question is

$$\mu' = cv_c l f(v/v_c l).$$

where c is a constant. This is, of course, in agreement with the value found for the roughened pipes, as in the latter case $f(v/v_c l)$ was a constant quantity for all values of v_c.

Table II.—Reduced Values of the Velocities in the two Smooth Pipes for Experiments in which $v_c l$ is constant (columns (1) and (2)) and v_c/l is constant (columns (1) and (3)).

Diameter 4·93 cm.		Diameter 7·4 cm.		
Radius.	Velocity in cm. per sec. (1)	Radius.	Velocity in cm. per sec. (2)	Velocity in cm. per sec. (3)
0	1525	0	1017	2215
0·45	1505	1·245	976	2120
0·70	1475	2·51	862	1892
0·96	1440	3·15	770	1693
1·21	1395	3·34	720	1605
1·47	1346	3·42	700	1556
1·72	1278	3·475	680	1510
1·97	1202	3·53	652	1453
2·10	1149	3·57	629	1407
2·23	1084	3·61	592	1344
2·28	1049	3·65	516	1248
2·32	1025	3·67	392	1098
2·35	984			
2·38	957			
2·41	908			
2·43	814			
2·44	592			

It appears, therefore, that the general character of the flow of air in pipes consists of a central region in which the ratio of the shearing stress to the rate of change of distortion is constant for any particular value of the flow, and that in the neighbourhood of the walls this alters rapidly until it becomes equal to the physical viscosity at the boundary.

In such a composite state of motion as this, it is clear that exact similarity over the whole section of the motions of air in two smooth pipes of different diameters can only exist when the values of both μ' and μ are the same for each. From the value of μ' here determined this condition can only be satisfied if the values of $v_c l$ and μ are the same for the two pipes. To illustrate this similarity, experiments were made on the distribution of velocity in the two smooth pipes used for this work and in which the centre filament velocities were respectively 1525 cm. per second in the 4·93 cm. pipe and 1017 cm. per second in the 7·4 cm. pipe. The experimental results for both pipes are given in Table II and are also plotted in fig. V, and it will be

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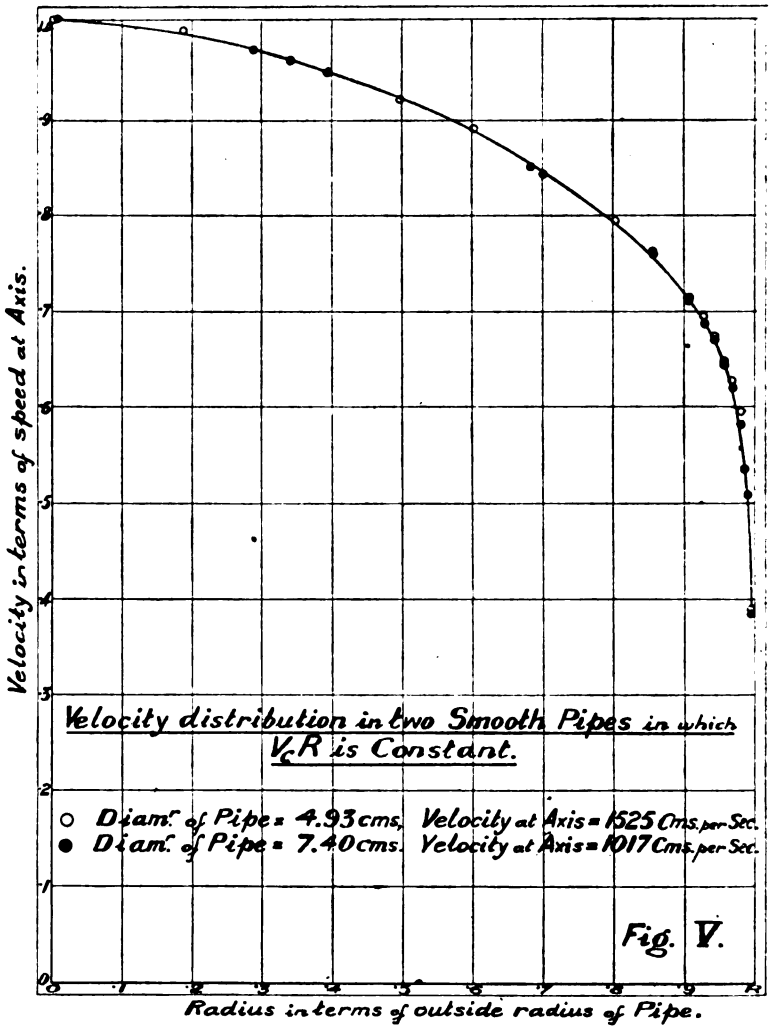
seen that, within the limits of accuracy of the observations, the curves are identical from the centre to the walls. It is evident, therefore, that in all questions of the prediction of the frictional resistance of bodies moving in fluids from experiments on small models of them, so long as the form of the function $f(\nu/v_c l)$ remains unknown, the only method of comparison is that in


Velocity in terms of speed at Axis.
Velocity distribution in two Smooth Pipes in which $V_c R$ is Constant.
○ Diam.r of Pipe = 4.93 cms. Velocity at Axis = 1525 Cms. per Sec.
● Diam.r of Pipe = 7.40 cms. Velocity at Axis = 1017 Cms. per Sec.
Fig. V.
Radius in terms of outside radius of Pipe.

which the value of $v_c l$ for the model is made the same as the corresponding quantity for the full-sized body.

The author desires to express his thanks to his colleague Mr. J. R. Pannell for the valuable assistance he has given in taking observations and reducing the results.

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Spectroscopic Investigations in connection with the Active Modification of Nitrogen.—I. *Spectrum of the Afterglow.*

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[Plate 10.]

Method of Observation.

The method of producing and isolating the nitrogen afterglow adopted in the observations dealt with in the present paper was that described by one of us in the recent Bakerian lecture.* A continuous stream of nitrogen was passed at low pressure through the exciting discharge tube, from which it was drawn into a side tube which was viewed end-on through a quartz window. The source of nitrogen was the commercial compressed gas, but it was purified to the required degree by passage through a tube containing chips of phosphorus and other tubes containing caustic potash and phosphorus pentoxide. The purer the nitrogen the more brilliant was the luminosity of the afterglow; a small amount of oxygen in the nitrogen sufficed to destroy the deep yellow glow, and only a bluish-white luminosity was then visible.

Three spectrographs have been employed in the investigation; (1) a small quartz spectrograph, giving a linear dispersion of 5·5 cm. from λ 7000 to λ 2200; (2) a larger quartz spectrograph giving 11·5 cm. for the same extent of spectrum; (3) a Littrow spectrograph, with a prism of light flint glass, giving 16 cm. for the region λ 7000 to λ 3800. For the determination of wave-lengths, comparison spectra of copper (with impurities of lead, etc.) were chiefly used.

General Description of the Spectrum.

As seen and photographed with instruments of small dispersion, the spectrum of the afterglow produced by the above method appears to be identical with that described by Lewis.† The luminosity, however, is so great, and its maintenance so easy, that considerable dispersion may be employed, and long exposures given, so that the spectrum can now be examined in much greater detail.

* R. J. Strutt, 'Roy. Soc. Proc.,' 1911, vol. 85, p. 219.

† 'Astrophys. Journ.,' 1904, vol. 20, p. 49.

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The spectrum may be conveniently considered to consist of three groups of bands, namely :—

Group α.—Three very conspicuous bands in the red, yellow, and green, with the brightest parts about wave-lengths 6252, 5804, and 5407. Another faint band about 5054 also belongs to this group.

Group β.—A series of 11 bands in the violet and ultra-violet, extending from 4312 to 2503. These are degraded towards the red, and have double heads. Other fainter series of bands of similar structure also belong to this group.

Group γ.—A series of flutings, degraded to the more refrangible side, corresponding in every particular with Deslandres' "third positive" group of nitrogen bands. These have double-double heads and extend from 3009 to 2155.

The stronger members of the second positive group of nitrogen bands (degraded to the violet, and extending from about 5000 to 3000) also appear in the spectrum of the afterglow, but they may have been introduced by internal reflections of the light from the exciting discharge tube, or by stray discharges in the afterglow tube itself, as Lewis did not find them by his method of observing the afterglow only when the discharge was interrupted. The first head of the cyanogen band at 3883 was also frequently present, but it may be accounted for by a slight carbon impurity,* and is not to be regarded as a part of the afterglow spectrum of pure nitrogen. The presence of carbon compounds was sometimes shown in another way by the strong line of carbon at 2478·7 in the spectrum of the discharge tube when the condenser was in circuit.

The Bands of Group α.

The three bands of group α, in the less refrangible part of the visible spectrum, are the most striking feature of the afterglow spectrum when the nitrogen is as pure as possible. Their true characters and relationships were not revealed until they were photographed with the comparatively great dispersion of the Littrow spectrograph. It was then found that their structure was identical with that of the "first positive" bands of nitrogen, and further investigation revealed the previously unsuspected fact that they are also identical in position with bands of nitrogen. This result is shown by the photographic comparison given in Plate 10, fig. 1, which indicates the extraordinary selection of first positive bands for special enhancement in the afterglow. It will be seen that the afterglow bands

* See Strutt, *loc. cit.*, p. 228.

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are not merely a survival of the brightest of the first positive bands,* but represent a special development of the more refrangible parts of the three groups into which the first positive spectrum is visibly divided.

The positions of the various bands are roughly shown by the wave-length scale marked on the photographs. Adopting Von Helm's values for the nitrogen bands,† the wave-lengths and oscillation frequencies of the first heads of the principal bands which occur in the afterglow spectrum are as indicated in Table I.

Table I.—The Visual Bands of the Afterglow (Group α).

	Wave-length.	Intensity.	Frequency *in vacuo*.	Frequency difference.	Second difference.
Red ...	6322·73	2	15812		
	6252·81	5	15989		
	6185·44	1	16163	1235	
Yellow	5854·69	4	17076		30
	5804·28	10	17224		
	5755·20	8	17371	1265	
Green	5442·25	1	18370		28
	5407·08	5	18489		
	5372·78	5	18607	1293	
Green	5053·6*	2	19782		
	5030·8*	2	19872		

* Measures by Hasselberg. Identified by visual observations.

The frequency differences and second differences for the strongest heads of the bands are given in the fourth and fifth columns of the table, and similar figures are obtained for the other corresponding heads. These differences are of interest as showing that the afterglow bands have not been selected at random from the numerous series which build up the first positive spectrum of nitrogen, but that they constitute three definite series of the usual character. They are, in fact, identical with three consecutive horizontal series in Cuthbertson's arrangement of the first positive bands of nitrogen in 13 series,‡ namely:—

* The faint bands less refrangible than 6322 shown in the photograph probably do not form part of the true afterglow spectrum, but represent part of the normal first positive spectrum accidentally superposed on that of the afterglow.

† Kayser's 'Handb. der Spectroscopie,' vol. 5, p. 828.

‡ 'Phil. Mag.,' 1902, [6], vol. 3, p. 348.

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	Series 3.	Series 4.	Series 5.	Series 6.	Series 7.
Series α_1	18370	17076	15812		
	1412	1413	1412		
Series α_2	19782	18489	17224	15989	
		1383	1383	1382	
Series α_3		19872	18607	17371	16163

The association of the bands in the afterglow suggests that of the various possible arrangements of the first positive bands the horizontal series in the above table are perhaps specially significant. It will be observed that, on the frequency scale, a displacement of one of the horizontal series by an appropriate amount will result in its superposition on one or other of the remaining series, thus resembling the five series into which the second positive bands of nitrogen have been divided by Deslandres.*

The relation between the bands is shown in another way by the application of Deslandres' general formula for the first positive bands,† namely :—

$$n = 22785{\cdot}1 - \frac{30{\cdot}319}{8}(2m)^2 + \frac{29{\cdot}363}{8}(2p+1)^2.$$

The first horizontal series of the above table is obtained when $m = 47$ and $p = 42, 43, 44$; the second when $m = 46$ and $p = 41, 42, 43, 44$; and the third when $m = 45$ and $p = 40, 41, 42, 43$. The bands shown in fig. 1*b* which are less refrangible than 6322 do not belong to either of these series, and, as already pointed out, they probably do not form part of the afterglow spectrum, but have been introduced by accident.

It thus appears that, in the less refrangible part of the spectrum, the afterglow shows no new bands, and only differs from that of the ordinary discharge through nitrogen in the concentration of the luminous energy into a small selection of the numerous series into which the first positive spectrum can be divided.

It should be noted also that the first positive bands of nitrogen are greatly reduced in intensity in the condensed discharge, which generates the afterglow, as compared with the uncondensed discharge, so that the partly abolished first positive bands may be considered to reappear in the afterglow, but with greatly modified intensities. Apart from the modification of intensities, for which we can offer no explanation at present, this observation is in accordance with the view that nitrogen is partially dissociated in the condensed discharge, and that the afterglow is produced during the re-formation of ordinary nitrogen.

* 'Comptes Rendus,' 1887, vol. 104, p. 972.

† 'Comptes Rendus,' 1902, vol. 134, p. 747.

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The Bands of Group β.

The general character of the second group of bands, designated the β group, will be gathered from Plate 10, fig. 2*b*. The positions of the brighter bands were only very roughly determined by Lewis, and it has been thought desirable to determine them with the considerable accuracy which is made possible by the use of the larger quartz spectrograph, and to include as many as possible of the fainter bands for the investigation of series relationships. The resulting wave-lengths for the principal series of bands, and their approximate intensities on a scale of 10 for the strongest, are shown in Table II, together with the oscillation frequencies *in vacuo*, and the first and second differences. The analysis of the intervals separating the bands suggests that the wave-lengths are correct to a few tenths of a tenth-metre.

Table II.—Group β Bands of the Afterglow.

Wave-length.	Intensity.	Frequency *in vacuo*.	Frequency difference.	Second difference.
4312·3		23183		
4296·5	1	23268		
			1547	
4042·8		24728		21
4028·7	2	24815		
			1568	
3801·9		26295		30
3789·3	4	26383		
			1598	
3584·7		27888		26
3572·9	6	27981		
			1624	
3387·2		29514		28
3376·8	9	29605		
			1652	
3207·4		31169		31
3198·4	10	31257		
			1683	
3043·2		32851		24
3035·0	10	32940		
			1707	
2893·0		34556		27
2885·4	9	34647		
			1734	
2754·5		36294		29
2747·9	7	36381		
			1763	
2626·9		38057		30
2620·9	4	38144		
			1793	
2509·0		39845		
2503·2	1	39937		

It will be seen that the bands form a well-defined series, with the strongest bands about the middle, as is often the case with band spectra.

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The average second difference is about equal to that which appears to be common to the first and second positive nitrogen series, but otherwise the series is quite distinct, and the bands have a structure which is different from that of any of the other bands attributed to nitrogen.

The oscillation frequencies of the more refrangible heads of the bands are closely represented by the formula

$$n = 13{\cdot}89\,m^2 - 18747,$$

where m has values ranging from 55 to 65. The calculated differ from the observed values by amounts which only once reach as much as three units.

In addition to this chief series of bands, there are several fainter ones of similar structure, particulars of which are given in Table III (see also Plate 10, figs. 2*b* and 3*b*). These also form series, which may be conveniently designated β_1, β_2, etc., as in the last column of the table. The intensities are roughly on the same scale as those of the main series in the previous table.

Table III.—Fainter Bands of Group β.

Wave-length.	Intensity.	Frequency *in vacuo*.	Series.	Wave-length.	Intensity.	Frequency *in vacuo*.	Series.
2951·2		33875		2558·0		39082	
2944·0	2	33958	β_1	2552·3	2	39169	β_1
2923·8		34192		2542·8		39315	
2916·2	2	34281	β_3	2537·1*	1	39404	β_3
2809·7		35581		2493·9		40086	
2802·7	2	35670	$_1$	2488·3	3	40176	β_2
2786·5		35877		2433·2		41086	
2780·1	2	35960	β_3	2428·2	3	41171	β_3
2732·2		36590		2387·0		41881	
2726·0	1	36673	β_2	2382·3	1	41964	β_2
2678·8		37319		2331·5		42878	
2672·9	3	37402	β_1	2326·8	2	42965	β_3
2608·6		38324		2236·1		44707	
2602·9	2	38408	β_2	2232·3	1	44783	β_3

* This head is hidden by the mercury line 2536·7, accidentally present, and its position has been estimated by consideration of the intervals separating the component heads.

These secondary series are related to the chief series and to each other in the same way that the constituent series of the first or second positive groups are related, such that a general displacement of one series by the proper amount will superpose it upon one of the other series. This is shown in the following arrangement of the frequencies:—

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	$m = 66$.	$m = 65$.	$m = 64$.	$m = 63$.	$m = 62$.	$m = 61$.	$m = 60$.
Series β ...		39937	38144	36381	34647	32940	31257
			1025	1021	1023	1018	
„ β_1 ...			39169	37402	35670	33958	
			1007	1006	1003		
„ β_2		41966	40176	38408	36673		
		999	995	998			
„ β_3 ...	44783	42965	41171	39404		35960	34281

It follows that the formula for the main series may be adapted to the secondary series by an alteration of one of the constants thus—

Series β_1 ..... $n = 13{\cdot}89\,m^2 - 17725$.

„ β_2 ..... $n = 13{\cdot}89\,m^2 - 16718$.

„ β_3 ..... $n = 13{\cdot}89\,m^2 - 15723$.

The values of m for the several vertical columns are shown in the tabular arrangement above. Series β_3 fails to show the band corresponding to $m = 62$ (λ 2653·8), although there is no other band at this place which could mask it.

The several series of group β must clearly be regarded as forming a connected system, but they have no evident relation to the other known series of nitrogen bands. As in the case of the α group, however, the β group does not represent a spectrum which exists exclusively in the afterglow. The stronger bands were observed faintly by Lewis in the ordinary discharge through nitric oxide, and our own experiments have indicated that they occur under suitable conditions in similar discharges through air or nitrogen. This is illustrated in the case of air in Plate 10, fig. 2*a*. The original negatives show the five strongest bands of group β (3377 to 2748) and the four bands of the series β_2, and it is remarkable that the latter are relatively more developed than the chief β series in the air discharge.

The bands of group β are found in association with the third positive bands of nitrogen, dealt with in the next section, and, as in the case of those bands, we have not found sufficient evidence to show that anything but nitrogen is necessary for their development.

The general result of the investigation of the β group of bands is to show that, like group α, they tend to disappear from the spectrum of the exciting discharge, and they reappear with somewhat modified intensities in the afterglow.

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The Bands of Group γ.

As already remarked, the third group of afterglow bands is identical with the third positive band spectrum of nitrogen. This is indicated by the photographs reproduced in Plate 10, fig. 3, which show the spectrum of the afterglow in comparison with that of air. For convenience of reference, the positions of the less refrangible heads, from the data given by Schniederjost,* are indicated in Table IV.

Table IV.—Chief Heads of Third Positive Bands of Nitrogen.

3009·55	2478·90
2859·80	2370·38
2722·43	2269·57
2595·80	2154·80

These bands occur strongly in several other sources besides the afterglow and the uncondensed discharge in air or nitrogen. They are found in the spectrum of an uncondensed spark in air at atmospheric pressure, in the arc between metallic poles, in the flame of cyanogen, and in the flame of ammonia burning in oxygen. Deslandres has suggested that they may be due to an oxide of nitrogen—developed by traces of oxygen in the case of a supposed nitrogen tube—as he found them to disappear from the spectrum when the nitrogen had been passed over heated sodium. The absence of the bands from the *condensed* discharge in nitrogen is also regarded by Lewis as favouring their oxide origin, the idea being that the bands vanish because of the decomposition of the compound which is thought to produce them.

We have not been able to convince ourselves, however, that these third positive bands require anything more than nitrogen for their production. With all precautions to exclude oxygen, the bands have always been present in the afterglow spectrum, even when the nitrogen was passed through melted phosphorus before it entered the discharge tube. In the discharge tube itself, it was found that the presence or absence of the bands seemed to depend only upon the intensity of the discharge. In the condensed discharge, and in the uncondensed discharge, if of sufficient intensity, the bands in question are wanting, but with other things remaining the same they made their appearance when the strength of the discharge was sufficiently reduced. It would thus appear that the third positive bands are more sensitive to changes in the discharge than the bands of the first and second positive groups, and are the first to be abolished as the discharge approaches that necessary to produce the line spectrum.

* 'Zeitsch. f. wiss. Photog.,' 1904, vol. 2, p. 265.

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The general behaviour of these bands in relation to the afterglow is very similar to that of the α and β groups. They occur in the uncondensed discharge, disappear in the stronger discharge which produces the afterglow, and reappear in the afterglow; they differ from the other two groups, however, in that there is no notable change in the relative intensities of the component bands.

Spectrum of Exciting Discharge.

It seemed important to compare the spectrum of the condensed discharge which develops the afterglow with that of the uncondensed discharge which ordinarily fails to do so. In the first place it was found that a discharge giving only the line spectrum does not excite the afterglow. A special tube was constructed with a very narrow capillary. The electrodes projected almost into this capillary, so as to avoid any development of the band spectrum in the wider parts of the tube, which might have made the result ambiguous. A current of pure nitrogen was passed through this tube, excited by the condensed discharge, but no afterglow was observed. The same current of rarefied nitrogen passed on its way to the pump through a wider discharge tube capable of giving the band spectrum. When the discharge was transferred to this tube, the afterglow was well developed. This served as a check, to prove that the failure to obtain the afterglow in the previous instance had not been due to any defect in the quality of the gas. It was accordingly only necessary to investigate the modifications of the *band* spectrum which occur in passing from a discharge of moderate intensity without condenser to a discharge with the condenser.

It was already known that the effect of the condenser is to reduce the intensity of the first positive bands, to brighten the second positive bands, and to abolish those of the third positive group. We have found in addition that a new series of seven bands in the ultra-violet appears in the spectrum of the condensed discharge. There appears to be no previous record of these bands in the observations made by Deslandres and others, but there seems to be no reason to doubt that they belong to nitrogen. For purposes of reference, this series may be conveniently called the "fourth positive" group of nitrogen.

As photographed with the larger quartz spectrograph (Plate 10, fig. 4*b*), each of the fourth positive bands shows five principal heads, of which the most refrangible is the strongest in each case, and the middle one next in order of brightness. The flutings are degraded towards the more refrangible end of the spectrum.

The wave-lengths of the bands, their relative intensities, oscillation frequencies, and frequency differences are shown in Table V.

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Table V.—Fourth Positive Bands of Nitrogen.

Wave-length.	Intensity.	Frequency *in vacuo*.	Frequency difference.	Second difference.	Remarks.
2903·9		34427			
02·0		449			
00·3	1	469			
2898·1		496	1561		
96·6		34513			
2777·9		35988		27	
76·5		36006			
75·1	2	024			Also a faint head at 2774·3.
72·8		054	1588		
71·4		36072			
2660·5		37576		28	
59·3		593			
57·9	5	613			Also a faint head at 2657·0.
55·8		643	1616		
54·5		37661			
2550·7		39192		30	
49·7		209			
48·4	8	229			
46·6		257	1646		Also a faint head at 2547·7.
45·3		39277			
2448·0		40838		31	
47·0		854			
45·6	10	878			Also a faint head at 2445·0.
44·0		905	1677		
42·8		40925			
2351·4		42515		27	
50·3		535			
49·0	6	559			
47·5		586	1704		
46·4		42606			
2260·8		44219			
59·6		242			This band is not very well defined on the photographs.
58·4	2	266			
57·1		291			
56·0		44313			

The structure of these bands is different from that of any belonging to the other groups of nitrogen, but a possible relation to the second positive bands is suggested by a consideration of their series relationships, and by the fact that both sets of bands are specially developed in the condensed discharge. The probable relation of the new bands to the second positive nitrogen group will be sufficiently indicated by the following comparison with Series III of the second positive spectrum. The oscillation frequencies (*in vacuo*) for the latter have been calculated from the wave-lengths given by Ames* :—

* 'Phil. Mag.,' 1890, [5], vol. 30, p. 48.

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2nd positive. Series III.	4th positive. First heads.	Difference.
23798	34427	10629
25357	35988	10631
26946	37576	10630
28562	39192	10630
30208	40838	10630
31882	42515	10633
33585	44219	10634

The difference is constant within the limits of error, and numerically, at least, the fourth positive bands are related to the second positive as the several series of the latter are related to each other. The figures in the first and second columns of the foregoing table may be respectively calculated from the formulæ

$$n = 14{\cdot}306m^2 - 17918,$$
$$n = 14{\cdot}306m^2 - 7288,$$

where m ranges from 54 to 60.

The fourth positive bands appear to be the most characteristic feature of the spectrum of the discharge which produces the afterglow, but a change of state in the nitrogen is also indicated by the modified intensities of the other three positive groups. The bands are also found, but with less intensity, in the condensed discharge through a tube containing air, and if they are characteristic of the afterglow-producing gas, it may be presumed, in accordance with other experiments, that the absence of the nitrogen afterglow in air tubes is due to the presence of oxygen.

Summary.

(1) The paper gives a detailed account of the spectrum of the afterglow of pure nitrogen, with wave-length determinations of sufficient accuracy to indicate the series relationships of the various bands.

(2) The characteristic bands of the afterglow in the red, yellow, and green are complex groups which have been found to be identical with some of the bands forming the sequence known as the first positive group of nitrogen. They represent a special development of three of the numerous series into which the first positive bands have been divided.

(3) The second group of afterglow bands, extending from 4312 to 2503, corresponds with a group of faint bands which occur in the uncondensed discharge in air or nitrogen, and the third group is identical with the third positive group of nitrogen bands, as previously shown by Lewis.

(4) The most characteristic feature of the condensed discharge which

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produces the afterglow is a series of seven complex bands, occupying the region 2904 to 2256, which have not previously been recorded as belonging to nitrogen. It is suggested that these should be designated the "fourth positive" group of nitrogen bands.

(5) No afterglow is excited when the discharge is such as to give only the line spectrum of nitrogen.

The authors are indebted to Mr. H. Shaw, A.R.C.S., for valuable assistance in the computation of wave-lengths, and in enlarging the photographs for reproduction.

DESCRIPTION OF PLATE.

1*a*. Uncondensed discharge in nitrogen, showing the first positive bands in the red, yellow, and green.

1*b*. Afterglow bands of Group *a*, showing relation to first positive bands.

2*a*. Uncondensed discharge in air, violet and ultra-violet region, showing second positive bands of nitrogen, part of the third positive group, etc.

2*b*. Afterglow bands of Group β, which are also seen faintly in the spectrum of air, 2*a*.

3*a*. Uncondensed discharge in air, ultra-violet region, showing the third positive bands of nitrogen, etc.

3*b*. Afterglow bands of Group β and Group γ (third positive nitrogen).

4*a*. Uncondensed discharge in nitrogen, ultra-violet region.

4*b*. Condensed discharge in nitrogen, which excites the afterglow, showing the new "fourth positive" bands.

1*a* and 1*b* were taken with the Littrow spectrograph and the remainder with the larger quartz spectrograph. The scales attached to the photographs are strictly only applicable to the upper spectrum in each pair, owing to difficulties of mounting.

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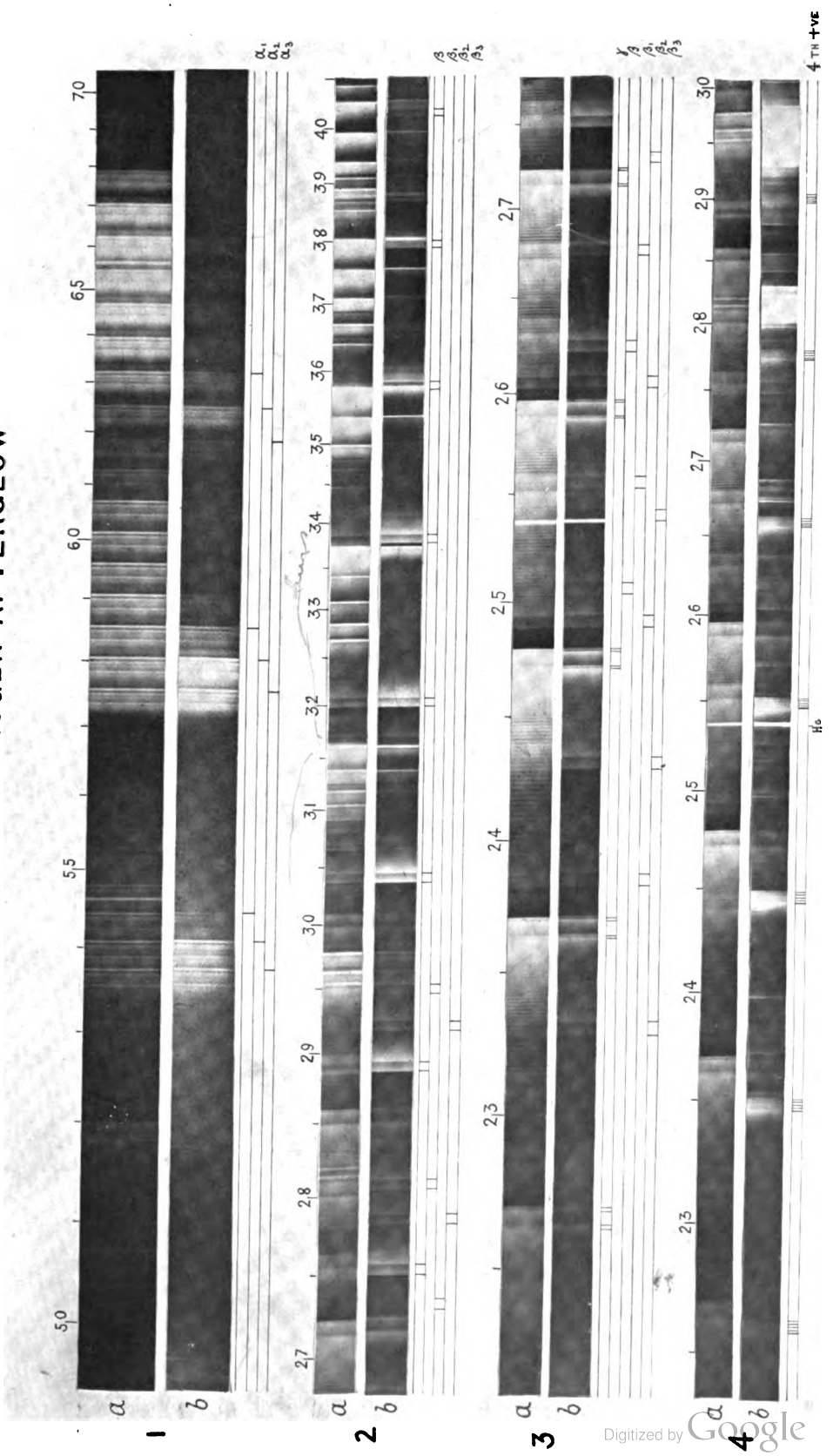

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The Constitution of the Alloys of Aluminium and Zinc.

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(Abstract.)

In connection with an extended research on the properties of the light alloys of aluminium, undertaken on behalf of the Alloys Research Committee of the Institution of Mechanical Engineers, the authors endeavoured to confirm the equilibrium diagram of the aluminium-zinc alloys published by Shepherd*; preliminary observations, however, showed that a redetermination of the diagram was required, and this is described in the present paper.

The alloys have been studied both thermally and microscopically. For the thermal investigation a large number of cooling curves and some heating curves were taken by means of a delicate potentiometer and a thermo-couple, large masses of alloy (300 grm.) and slow rates of cooling being employed. The information thus obtained was supplemented by additional cooling curves taken on specimens of certain of the alloys which had been exposed to prolonged heating (up to 100 hours) in order to allow of the completion of gradual chemical changes.

The microscopic examination of the alloys was applied to specimens which had been (*a*) slowly cooled from fusion, (*b*) annealed at certain definite temperatures and slowly cooled, and (*c*) annealed at certain temperatures and then quenched. In addition, the method of microscopic examination of small quenched specimens has been used in order to locate the solidus curve of the alloys.

The equilibrium diagram arrived at by the authors, which differs materially from that hitherto accepted, is shown in the accompanying figure, where both cooling curve and quenching observations have been plotted in the usual manner on percentage concentration as abscissæ and temperatures as ordinates. The liquidus of the alloys is represented by the lines ABCD; these correspond closely with the liquidus as drawn by Shepherd, except for the break at the point C; the authors regard the existence of this break as being well established both by the observations as plotted and by corroborative evidence for the existence of a definite compound Al_2Zn_3. The point B is a eutectic point corresponding to a concentration of 95 per cent. of zinc. The solidus of these alloys is given by the lines AEBFGHD.

* 'Journal of Physical Chemistry,' 1905, vol. 9, p. 504.

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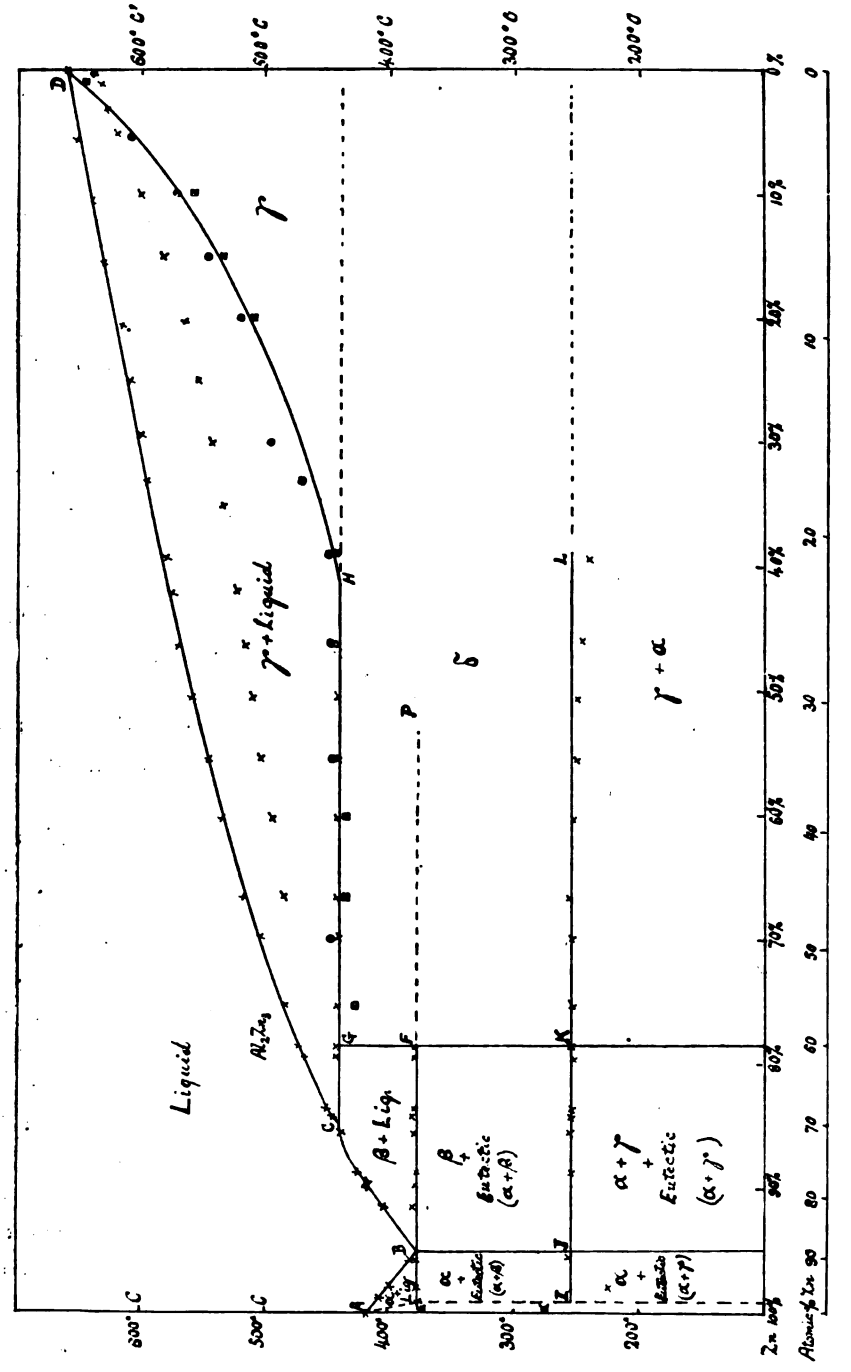
Alloys containing more than 95 per cent. of zinc commence to solidify along the line AB by depositing crystals of the α-phase, which consists of



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zinc holding in solution less than 1 per cent. of aluminium. On the line EB the solidification is completed by the freezing of the residual liquid as eutectic. The distance of the point E from the zinc end of the diagram has not been definitely fixed, but it is found to be less than 1 per cent. In the field EBJI the alloys consist of crystals of α embedded in a solid eutectic of α and β. Along the line IJ, β undergoes a decomposition into two phases, which have been found to be α and γ, so that below IJ these alloys consists of α and γ only. The change $\beta = \alpha + \gamma$ is, however, a slow one and is not completed in alloys cooled at any ordinary rate. Alloys in the field BCGF consist of a mixture of crystals of β and liquid; at the line BF this liquid solidifies in the form of eutectic, and in the field BFKJ the alloys consist of crystals of β embedded in a solid eutectic of β and α; at the line JK, the β-phase again decomposes into α and γ, the change now taking place in both the primary crystals of β and in the β-constituent of the eutectic. In the field CGHD the alloys consist of crystals of solid γ surrounded by liquid, the γ-phase being simply a solid solution of zinc in aluminium. Along the line CGH the solid γ reacts with the liquid to form the β-phase, according to the equation

$$\gamma + \text{liquid} = \beta.$$

Quenching experiments have shown that to the right of the line FG the alloys become completely solid along the line GH; this indicates that at the concentration of the line GF the above reaction just absorbs the whole of the liquid still present at that temperature. Cooling curves of alloys to the right of the line GF still show the eutectic arrests along the dotted line FP, but after prolonged heating at a temperature just below that of the line GH these arrests disappear. The exact position of the line GFK has been fixed by two further series of determinations; by estimating the quantities of heat generated by the solidification of the eutectic along the line BF, it has been possible to find the end point of the eutectic line by extrapolation, while a similar estimation in regard to the reaction along the line JKL has furnished the position of the maximum intensity of that reaction. Within the limits of experimental error of such determinations, these two series agree in fixing the position of the line GFK at or close to 78 per cent. of zinc, and this corresponds to the compound Al_2Zn_3 (78·35 per cent. of zinc). The microstructures of the alloys containing this phase (called β in the diagram) show characteristic dendritic crystals which possess a marked habit of assuming six-rayed forms, such forms being very unusual in metals. It should be added that a quantitative connection between the heat evolutions along the lines CGH and JKL has been established, so that the authors draw the conclusion that the upper of these two series of reactions represents the formation and the lower the decomposition of the compound Al_2Zn_3.

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To the right of the line GFK the reaction γ+liquid = β leaves an excess of γ, but, microscopically, alloys within the field DGKL are found to be homogeneous under equilibrium conditions; it follows that β and γ form a continuous series of solid solutions. Of this series, those rich in β show the heat evolution due to the decomposition of β along the line KL, but special circumstances render it difficult to determine microscopically where the limit of this decomposition lies. It is also doubtful whether the reaction which results in the formation of the compound β takes place if the whole of the metal has solidified before the temperature of CGH has been reached. The lines CGH and JKL have therefore been continued towards the aluminium end of the diagram as dotted lines only.

The decomposition of β along the line JKL gives rise to an interesting duplex micro-structure, particularly to the right of K, where the decomposition is that of the solid solution of γ in β, called δ in the diagram. The alloys appear perfectly homogeneous when quenched from temperatures above the line KL, but if slowly cooled through that line, and, still more, if annealed for a time, first at a temperature just below GH, and then again at a temperature just below KL, they exhibit a laminated duplex structure closely resembling the laminated structures met with in the "pearlite" of annealed carbon steels. Such a laminated structure resulting from the decomposition of a solid solution has not, so far as the authors are aware, been hitherto met with except in the iron-carbon alloys.

The position of the line HD has been ascertained by a series of quenching experiments; the quenching temperatures which still allowed signs of the presence of liquid to be detected in the specimens are indicated by dots surrounded by small circles, while those in which no liquid could be traced are shown as small squares.

A further line of arrest-points, which, although minute, are well marked and of constant occurrence, are shown in the regions of γ and γ+liquid. The authors cannot assign an explanation for these points on the basis of a diagram of binary alloys, and are therefore driven to the suggestion that they may be due to the action of a third component entering into the alloys in minute quantities as an impurity. Iron and silicon are found in the alloys in small quantities (under 0·2 per cent.), and this may be connected with the occurrence of these small heat evolutions.

The authors desire to express their thanks to various members of the staff of the Metallurgy Department of the National Physical Laboratory who have assisted in the work of this research, and to the Director, Dr. R. T. Glazebrook, F.R.S., for his interest in its progress.

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On the Anode and Cathode Spectra of Various Gases and Vapours.

By G. Stead, B.A., Formerly Scholar of Clare College, Cambridge.

(Communicated by Prof. Sir J. J. Thomson, F.R.S. Received March 21,—Read June 1, 1911.)

In many gases the colour of the glow surrounding the cathode of a vacuum tube is markedly different from that of the positive column, and there are corresponding differences in the spectra of these two regions. Some years ago Prof. Sir J. J. Thomson* examined systematically a number of compounds from this point of view, and found that electro-positive elements had a tendency to appear at the cathode, whilst electro-negative elements showed a preference for the anode. In explanation of these facts he supposed that a process of the nature of electrolysis went on in gases under the influence of the electric discharge, resulting in the liberation of ions in the neighbourhood of the two electrodes. The present paper gives an account of work which I have been carrying on lately in the Cavendish Laboratory, and which is a continuation and extension of what has previously been done.

The discharge tube used was of the form shown in fig. 1. Its length was

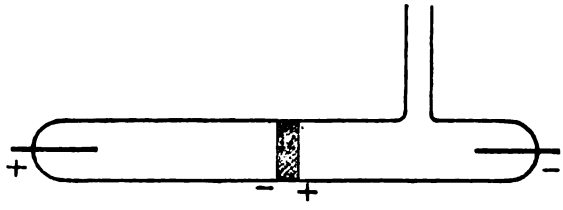

Fig. 1.

approximately 25 cm., whilst different diameters were tried, varying from about 0·3 cm. to about 1 cm. It was divided into two halves by a small plate of aluminium (about 0·5 cm. thick) which fitted sufficiently well to cause the discharge to go through it and not round it. In these circumstances, one side of the plate forms an anode and the other a cathode, so that a small shift, either of the tube or of the spectroscope, suffices to bring one or the other electrode before the slit. A Cox induction coil was used, and in order to minimise the effect of reversals a "point and plane" spark-gap was placed in series with the discharge tube. Part of

* "On the Electrolysis of Gases," 'Roy. Soc. Proc.,' 1895, vol. 58.

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the work was carried out with an ordinary two-prism spectroscope, the rest with a Hilger constant deviation wave-length spectroscope. In every case observations were taken over as large a range of pressures as was practicable (0·01 cm. to 1 cm., roughly).

I. *Discharge through an Elementary Gas.*

That the two band spectra of nitrogen which appear, the one at the positive and the other at the negative pole, are entirely different, is too well known to require more than a passing mention. Oxygen shows a similar behaviour. Characteristic differences are also to be found in pure hydrogen. The gas was prepared—

1. By the action of caustic potash on aluminium.
2. By acting on pure zinc with dilute sulphuric acid containing a little copper sulphate.
3. By the electrolysis of a dilute solution of barium hydroxide.

Whatever the source of the hydrogen, it was always found that the "four-line" spectrum was bright at the cathode and faint at the anode, whilst the secondary spectrum showed much more strongly on the positive than on the negative side of the plate. Further, the intensity of the blue line ($H\beta$) relative to the red line ($H\alpha$) was much less at the anode than at the cathode.

Various observers* have shown that the appearance of the secondary spectrum is favoured by a weak discharge, *i.e.* by a low (electrical) temperature. It is thus not improbable that the preference of the secondary spectrum for the anode is due to the smallness of the potential gradient, as compared with the corresponding gradient at the cathode.

II. *Discharge through Compound Gases and Vapours.*

(i) *Hydrogen Chloride.*—The gas was prepared by the action of concentrated sulphuric acid on ammonium chloride, and was dried by means of strong sulphuric acid and phosphorus pentoxide.

At the cathode the four-line spectrum of hydrogen showed brilliantly, accompanied by faint chlorine lines, whereas at the anode the spectrum of chlorine was bright and that of hydrogen faint. Further, on suddenly reversing the coil, the spectra did not alter immediately. For a second or so chlorine was bright at the new cathode (the old anode) and hydrogen at the new anode, and the change to the fresh conditions took an appreciable time.

* B. Hasselberg, 'Mem. de l'Acad. de St. Petersbourg' (vii), vol. 31, p. 14; M. A. Dufour, 'Ann. de Ch. et de Ph.' (3), 1906, vol. 9, p. 361.

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These facts seem to be explained very well by Prof. Sir J. J. Thomson's hypothesis of electrolysis. The lingering of the spectra on reversal is to be regarded simply as a manifestation of polarisation at the electrodes.

When the discharge was kept running continuously the chlorine was rather rapidly absorbed, presumably by the aluminium electrodes.

It is most important that the hydrogen chloride should be absolutely pure, otherwise the effects just described will not be observed. The required degree of purity is by no means a simple matter to obtain. A very small trace of carbon results in the appearance of the carbonic oxide spectrum throughout the positive column, and the chlorine lines, together with the hydrogen, occupy the negative glow.

The effect of a "flash discharge" was also tried. This was obtained by suddenly discharging a battery of Leyden jars through the spectrum tube. It was found that, in these circumstances, no separation occurred. Such a result is to be expected, as a flash discharge is of such short duration that there is no time for any structure to be set up in the tube.

(ii) *Chloroform.*—Liquid chloroform was admitted into a bulb which had been exhausted as completely as possible, and from this the vapour was drawn off as required.

On first passing the discharge the lines of hydrogen and chlorine appeared together at the cathode, whilst at the anode was found the so-called carbonic oxide spectrum (the appearance of which cannot be taken as trustworthy evidence of the occurrence of carbon monoxide). After the discharge had been running for (say) half-an-hour the chlorine lines became faint. It would seem, however, that the chlorine was still there, for a Leyden jar brought it out strongly at both electrodes.

Chloroform is apt to decompose under the action of the discharge, for a reason which is very obscure. Sometimes decomposition occurs in a couple of minutes, at other times the coil can be run for two or three hours without visible decomposition, and then suddenly, for no obvious cause, carbon begins to be deposited, and in a couple of minutes decomposition seems to be complete. No effect beyond brightening the spectra was produced by increasing the strength of the discharge. After decomposition had taken place the ordinary spectrum of hydrogen was found at the cathode, and the secondary at the anode. This implies simply hydrogen in the tube.

(iii) *Carbon Tetrachloride.*—This substance, like chloroform, showed a line spectrum of chlorine at the cathode, whilst carbonic oxide bands appeared at the anode. There was no decomposition with deposition of carbon.

(iv) *Silicon Tetrachloride.*—At first there was a bright continuous spectrum

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at both poles, but after about a minute silicon lines (with faint chlorine) appeared at the anode, and bright chlorine lines, but no silicon, at the cathode.

(v) *Stannic Chloride.*—The anode showed a line spectrum of tin, whilst at the cathode the same spectrum appeared, but accompanied by chlorine lines. Stannic chloride thus behaves much more like the tetrachlorides of carbon and silicon than a metallic chloride. This is strictly in accordance with chemical evidence, for the product of the action of water on stannic chloride is not a basic hydroxide but an acid—stannic acid, analogous to silicic and carbonic acid.

(vi) *Benzene.*—No separation could be obtained of the hydrogen, which showed faintly on both sides of the plate. Initially both electrodes showed the Swan bands with traces of the carbonic oxide spectrum, but the former was replaced by the latter very rapidly (say in 30 seconds) at the cathode, whilst a similar change took place more slowly (in about 10 minutes) at the anode. Carbon was deposited in large quantities on the walls of the tube and on the electrodes.

(vii) *Chlorobenzene.*—This, like benzene, showed no separation of the hydrogen. Chlorine lines appeared rather faintly at the cathode, but the anode gave no indication of their presence. Both sides of the plate showed bright carbonic oxide bands, and there were traces of the Swan spectrum at the positive pole at first. Decomposition took place very readily, with deposition of carbon.

(viii) *Carbon Disulphide.*—When the coil was run in the ordinary way with a hammer break the carbonic oxide spectrum appeared at both electrodes, with traces of the Swan spectrum at first. The vapour decomposed very easily and blackened the walls of the tube. If, however, a Wehnelt interrupter were substituted for the hammer break, so that a very bright discharge was obtained, at the cathode the carbonic oxide spectrum still remained, whilst at the anode it was replaced by the band spectrum of sulphur. Further, on reversing the coil, the spectra did not change suddenly.

It is worthy of note that with the Wehnelt interrupter no carbon was deposited on the walls of the tube. On the contrary, a deposit obtained by using the hammer break could be gradually removed by employing a Wehnelt interrupter. This is doubtless associated with the endothermic character of carbon disulphide.

(ix) *Hydrogen Sulphide.*—The gas was prepared by warming pure barium sulphide (Kahlbaum) with dilute hydrochloric acid.

With the hammer break the positive pole showed the sulphur band

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spectrum for about half a second after the coil was turned on, but it was very rapidly replaced by the spectrum of hydrogen. The negative pole gave the hydrogen spectrum always, and the difference between the anode and cathode was that which is characteristic of pure hydrogen. If the discharge were now stopped, and the tube allowed to "rest" for at least half a minute, then, on turning on the coil, the sulphur bands again flashed out for an instant at the anode. Apparently this could be repeated indefinitely.

If a strong discharge were sent through the tube by making use of the Wehnelt interrupter, the sulphur bands appeared permanently at the anode, whilst at the cathode hydrogen occurred as before. The spectra did not change quite suddenly when the coil was reversed.

(x) *Sulphur Dioxide.*—At the negative pole a line spectrum was observed, which was found to be identical with that obtained when a Leyden jar discharge is sent through sulphur vapour at low pressure. The light at the positive pole was bright blue in colour; it resolved into a continuous spectrum occupying the region between the yellow and the violet. There seemed no ground, however, for identifying it with the continuous spectrum given by oxygen.

(xi) *Hydrogen Bromide.*—The gas was prepared by running first a little water and then pure bromine into an exhausted bulb containing red phosphorus. It was then passed through red phosphorus, calcium chloride, and phosphorus pentoxide.

Hydrogen bromide did not behave at all as would be expected from analogy with hydrogen chloride. There was, in fact, little separation of the spectra at all, bromine and hydrogen lines being bright at both electrodes. The gas decomposed quite easily and the bromine disappeared.

It seemed possible that the anomalous behaviour of hydrogen bromide was associated with its rapid decomposition under the influence of the discharge, and arrangements were therefore made to allow of a continuous flow of the gas through the tube. This was accomplished by means of the apparatus shown in fig. 2. The discharge tube was made as symmetrical as possible so that there should be no appreciable difference of pressure between the two electrodes. The gas to the left of the tap (fig. 2) was at a pressure approximating to atmospheric, and it was allowed to stream through the fine capillary. After sweeping past the electrodes it was absorbed mainly by solid potash, the residue being taken up by charcoal and liquid air.

At pressures of the order of 1 cm. it was found easy to obtain the normal separation, *i.e.* hydrogen chiefly at the cathode and bromine mainly at the anode. At pressures of about 0·1 cm. or less separation could not be obtained, probably because the rate of flow was too small.

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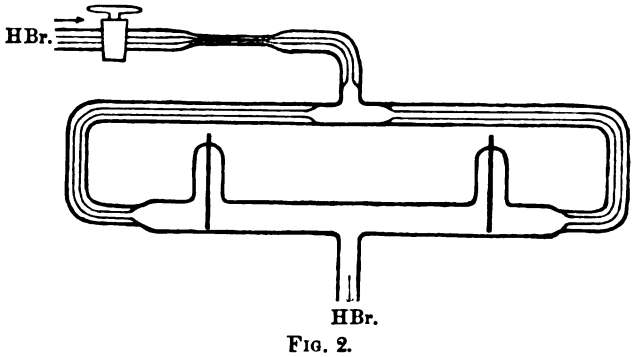

Fig. 2.

(xii) *Hydrogen Iodide.*—This gas was generated and purified in a manner analogous to that employed for hydrogen bromide, and was found to exhibit the same anomalous behaviour. There can be little doubt that the cause is the same in the two cases, and that separation would be obtained with hydrogen iodide, provided that a sufficient rate of flow was kept up.

(xiii) *Ethyl Bromide.*—At first the Swan spectrum was seen at both poles, accompanied chiefly at the cathode by the spectra of bromine and hydrogen. After a few seconds the Swan bands at the negative pole were replaced by carbonic oxide, and the same tendency was observable at the anode, except that the time required for the change was considerably greater. This time depends on the initial pressure. After the change the bromine lines began to disappear, apparently owing to absorption of the bromine. Finally the carbonic oxide spectrum appeared at both poles, accompanied by hydrogen at the cathode. Carbon was deposited gradually on the walls of the tube.

(xiv) *Methyl Iodide.*—At first the cathode showed hydrogen and iodine lines, and the anode iodine only. In a short time the iodine disappeared from the cathode, whilst carbonic oxide became visible at the anode. Carbon was deposited on the walls of the tube.

That the iodine really showed a preference for the anode was demonstrated by taking a symmetrical tube (fig. 3) provided with mercury electrodes. On

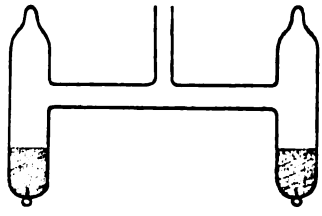

Fig. 3.

passing the discharge sublimates of mercury formed on the walls near the electrodes, and after about half-an-hour's running the sublimate close to the

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anode was brick red in colour (due to mercuric iodide), whilst the one near the anode was but little changed. A similar experiment was tried with hydriodic acid, but in this case both sublimates became brick-red in colour.

(xv) *Cyanogen.*—The gas was generated by heating a dry mixture of mercuric chloride and potassium cyanide, and dried over calcium chloride and phosphorus pentoxide.

Owing to the very rapid polymerisation of cyanogen it is most troublesome to work with, as the paracyanogen formed is deposited on the walls of the tube and renders them opaque. In the first experiment, it was found that the spectrum was the same all along the positive column. Hence, in subsequent work, an "end-on" tube was employed, which obviated the difficulty due to polymerisation.

When the coil was turned on, the characteristic cyanogen bands appeared for a few seconds at both poles, but were soon replaced by the spectra of nitrogen and carbonic oxide on both sides of the plate. The positive pole spectrum of nitrogen appeared at the anode, and the negative pole spectrum at the cathode.

(xvi) *Hydrocyanic Acid.*—At the cathode there were bright hydrogen lines and faint cyanogen bands, whilst at the anode the cyanogen spectrum was bright and that of hydrogen faint. Hence, the hydrogen showed a preference for the cathode, and the cyanogen group for the anode; in other words hydrogen cyanide behaved in a manner precisely similar to that of its analogue hydrogen chloride.

General Remarks.—It has been found that, whereas in hydrogen chloride the chlorine goes to the anode, in chloroform, carbon tetrachloride, etc., hydrogen and chlorine both appear at the negative electrode. These facts, at first sight contradictory, are in reality exactly what is to be expected from chemical evidence, if the appearance of a spectrum at a particular pole be in any way associated with the electro-chemical character of the atoms in question.

In hydrochloric acid chlorine is a typical electro-negative element, and carries a charge of opposite sign to that of the hydrogen. Chloroform and carbon tetrachloride, on the other hand, are formed by the direct replacement of hydrogen in methane by chlorine. Hence, it seems likely that in these compounds chlorine carries a charge of the same sign as that of the hydrogen which it replaces, *i.e.* a positive charge. When we come to chlorobenzene, the evidence obtainable from chemistry that the chlorine is behaving as an electro-positive element is very much stronger. Thus, if a monosubstitution product of benzene be nitrated, the particular isomeride obtained depends on the character of the first substituting group. When the latter is of an electro-

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negative character, the resulting disubstitution product is chiefly *meta*; if, on the other hand, it is of an electro-positive nature, the principal product is *para*. For instance, nitrobenzene yields on nitration meta-dinitrobenzene, whereas aniline gives para-nitraniline. If now chlorobenzene be nitrated, the chief product is para-nitrochlorobenzene, and not the meta-compound. Hence, the chlorine behaves like the *amido*-group, and not like the *nitro*-group; in other words, it is functioning as an electro-positive element, and not as an electro-negative one. This would seem to be as strong as it is possible for chemical evidence to be. Stannic chloride and silicon tetrachloride also give the results to be expected on chemical grounds. Hence, the fact that chlorine goes to the cathode in chlorobenzene, etc., so far from disproving the idea that the appearance of an element at a particular electrode is associated with its electro-chemical character, affords a very strong indication of the general correctness of this view.

Again, in the case of carbon disulphide and hydrogen sulphide, the sulphur appeared only at the anode, whereas in sulphur dioxide a sulphur spectrum was seen only at the cathode. Sulphur is electro-negative to hydrogen and carbon, but electro-positive to oxygen.

There seems good reason to conclude that, as in the case of liquid electrolysis, electro-positive elements tend to appear at the negative pole, and *vice versâ*. This, of course, does not necessarily mean that conduction in gases is purely electrolytic (*i.e.* subject to Faraday's laws). Indeed, the evidence from other sources against such a view is overwhelming. But because pure electrolysis cannot occur, it is not justifiable to assume that the electro-chemical character of the elements has no influence on the distribution of spectra in a discharge tube.

On the other hand, since many elementary gases show different spectra at the two electrodes, and since any explanation of the electrolytic type is difficult in this case, it seems probable that there are other factors involved. It appears to me probable that the difference in potential gradient and temperature at the two electrodes must not be lost sight of in framing an hypothesis to account for the facts described in this paper.

Summary.—The examination of a considerable number of gases and vapours has shown that the spectra of electro-negative elements tend to appear at the anode, whilst the spectra of electro-positive elements show a preference for the cathode.

The explanation of these facts is most likely to be found in—

(i) The difference in potential gradient and temperature at the two electrodes.

(ii) The electro-chemical properties of the elements concerned.

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In conclusion, I wish to express my most sincere thanks to Professor Sir J. J. Thomson, at whose suggestion this research was undertaken, and who has throughout given much encouragement by showing a never-failing interest in the progress of the work.

On a Class of Parametric Integrals and their Application in the Theory of Fourier Series.

By W. H. Young, Sc.D., F.R.S.

(Received April 19,—Read June 29, 1911.)

§ 1. The theorem commonly known as Parseval's Theorem, which, in its latest form, as extended by Fatou,* asserts that if $f(x)$ and $g(x)$ are two functions whose squares are summable, and whose Fourier constants are a_n, b_n and α_n, β_n, then the series

$$\tfrac{1}{2}a_0\alpha_0 + \sum_{n=1}(a_n\alpha_n + b_n\beta_n)$$

converges absolutely and has for its sum

$$\frac{1}{\pi}\int_{-\pi}^{\pi} f(x)\,g(x)\,dx,$$

must be regarded as one of the most important results in the whole of the theory of Fourier series.

I have recently, in the 'Proceedings' of this Society and elsewhere, had occasion to illustrate its usefulness, as well as that of certain analogous results to which I have called attention. They may be said, indeed, to have reduced the question of the convergence of Fourier series to the second plane. If we know that a trigonometrical series is a Fourier series, it is in a great variety of cases, embracing even some of the less usual ones, as well as those which ordinarily present themselves, all that we require. It has seemed to me, therefore, worth while to add another to the list of these results. This is the main object of the present paper, in which it is shown that if one of the functions has its $(1+p)$th power summable and the other its $(1+1/p)$th power summable, where p is any positive quantity, however small, then the above theorem is true with this modification, provided only the series in question is summed in the Cesaro way. In particular, the equality always holds in the ordinary sense whenever the series does not oscillate.

* Fatou, "Séries Trigonométriques et Séries de Taylor," 'Acta Mathematica,' 1905, vol. 30.

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I have, however, treated this problem as a part of a larger one, and have shown that the cosine series whose typical coefficient is $(a_n\alpha_n + b_n\beta_n)$, and the sine series whose typical coefficient is $(a_n\beta_n - b_n\alpha_n)$ are, under the circumstances stated, the Fourier series of continuous functions.

I have also shown this to be the case when one of the functions is bounded and the other summable. When the bounded function has also bounded variation, they are the Fourier series of functions of bounded variation.

All the previously known results,* as well as that above stated, follow at once as simple corollaries. Moreover, the question of the convergence of the series

$$\tfrac{1}{2}a_0\alpha_0 + \sum_{n=1}(a_n\alpha_n + b_n\beta_n) \quad \text{and} \quad \sum_{n=1}(a_n\beta_n - b_n\alpha_n),$$

as well as of other series obtained by ascribing particular values to x in the Fourier series in question, is made to depend on the examination of certain parametric integrals at the point in question.†

§ 2. We first prove an auxiliary theorem in the theory of sets of points.

Theorem.—*If* G *is a closed set of points of positive content* E *in the interval* (a, b), *and* G_x *is the set got by simply translating the set* G *a distance* x *in the direction* a *to* b, *then the sets* G *and* G_x *have a common closed set of points, whose content differs from* E *by less than an assigned quantity* e, *provided only* x *is less than a quantity* X *which can be specified.*

Suppose the black intervals of the closed set G arranged in any order, $d_1, d_2 \ldots, d_n \ldots$

Let e' be any chosen positive quantity less than e, and let R_m denote the sum of all but the first m of the black intervals, where m is the first integer for which

$$R_m < e'. \tag{1}$$

We then take X to be the largest quantity satisfying the two inequalities

$$X \leq (e - e')/(1 + m), \tag{2}$$

$$X \leq d_n, \qquad (n \leq m). \tag{3}$$

* For these results see my paper "On the Integration of Fourier Series," 'Lond. Math. Soc. Proc.,' 1910, Series 2, vol. 9, pp. 449–462.

† The method, as has been kindly pointed out to me, is not quite new. A particular case of our parametric integral was employed by A. C. Dixon in 1909, for the purpose of proving Fatou's Theorem, in a paper entitled "On a Property of a Summable Function," 'Camb. Phil. Soc. Proc.,' vol. 15, pp. 210—6. In reference to this proof it may be noted that no use is there made of the property of a Fourier series of never diverging properly, provided the Fourier function is continuous. In consequence the assumption has to be made that the series $\Sigma(a_n^2 + b_n^2)$ is known to converge to a sum not greater than the quantity to which it is to be proved equal. I notice that in Dr. Dixon's ingenious proof of the continuity of the parametric integral considered by him, the tacit assumption is made that Schwarz's inequality is true of Lebesgue improper integrals, a result which had not at that time been proved.

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Now, by reason of the inequality (3), when we translate the interval (a, b) carrying the set G and its black intervals, each of the black intervals d_n, with index not greater than m, will have in common with itself, after translation, a part of length $(d_n - x)$, x denoting the amount of translation. Thus there will be at least m such common parts of intervals containing no point of G either before or after the translation. Hence, if we denote by I the content of the closed set, consisting of all the points of G before and after translation,

$$\begin{aligned} \mathrm{I} &\leq b-a+x-\sum_1^m (d_n-x), \\ &\leq b-a+x+mx-\sum_1^m d_n, \\ &\leq \mathrm{E}+\mathrm{R}_m+(1+m)x, \\ &< \mathrm{E}+e, \end{aligned} \tag{4}$$

using (1) and (2).

Now, if I_1 and I_2 are the content of two closed sets, I that of the set consisting of both sets, and I′ that of their common part, we have*

$$\mathrm{I}_1+\mathrm{I}_2 = \mathrm{I}+\mathrm{I}'. \tag{5}$$

In our case $\mathrm{I}_1 = \mathrm{I}_2 = \mathrm{E}$. Hence by (4) and (5),

$$\mathrm{I}' > \mathrm{E}-e. \quad \text{(Q.E.D.)}$$

Cor.—*The same is true if, in the above enunciation, we omit throughout the word "closed."*

For, in this case, we can find a closed component of G, say G′, whose content differs from E by less than $\frac{1}{2}e$. Also, by the theorem, we can determine X so that, for any value of x less than X, the common points of G′ and G'_x, *a fortiori* the common points of G and G_x, form a set whose content differs from that of G′ by less than $\frac{1}{2}e$, and therefore from that of G by less than e.

§ 3. The necessary and sufficient condition that a function $\mathrm{F}(x)$ should be an integral† has been stated by Vitali in a form which it will be convenient to modify slightly for the purposes in hand. From Vitali's condition we know that, if $f(x)$ is a summable function, and e a chosen positive quantity, we can find E so that, if D denote any set of non-overlapping intervals of content less than E, $\int_{\mathrm{D}} f(x)\,dx$, which is the increment of the integral over the set of intervals D, is numerically less than e. But we also know‡ that,

* Young's 'Theory of Sets of Points,' Cambridge University Press, 1906, p. 84.

† See my paper on "Semi-integrals and Oscillating Successions of Functions," 'Lond. Math. Soc. Proc.,' 1910, Series 2, vol. 9, p. 291, *seq.*, where also references will be found.

‡ *Loc. cit.*, p. 291.

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if G is a measurable set of points of content less than E, we can find a sequence of sets of intervals D_1, D_2,..., D_n,... having the points of G as common points, and no other common points, except possibly a set of content zero, and that $\int_G f(x)\,dx$ is the unique limit of $\int_{D_n} f(x)\,dx$, when n increases indefinitely. Since the content of D_n has that of G as limit, it must be less than E, when n is large enough; thus, by Vitali's property, $\int_{D_n} f(x)\,dx$ becomes eventually less than e, and therefore its unique limit, $\int_G f(x)\,dx$, is also less than e. Thus we have the following property of a summable function, which we shall need in the sequel:—

If $f(x)$ is a summable function, and e a chosen positive quantity, we can find E, *so that the integral of $f(x)$ over any and every set of points of content less than* E *is less than e.*

§ 4. Theorem.—*If $f(t)$ is a summable function, and* G *a set of positive content, $\int_G f(x+t)\,dt$ is a continuous function of x.**

For if, as in § 2, G_x denote the set got by translating the set G a distance x, and I′ denote the common part of the sets G and G_x, we have seen that the remaining components E and E_x of G and G_x have content less than e, provided $|x|$ is less than a certain quantity X, which can be specified. Moreover, by the fundamental property of an integral, the quantity e, here used, may be so chosen that the integral of $f(t)$ over any and every set of content less than e is numerically less than a positive quantity e' chosen at will. This being so, we have

$$\int_E f(t)\,dt < e', \qquad \int_{E_x} f(t)\,dt < e',$$

while
$$\int_G f(t)\,dt = \int_{I'} f(t)\,dt + \int_E f(t)\,dt,$$

and
$$\int_G f(x+t)\,dt = \int_{G_x} f(t)\,dt = \int_{I'} f(t)\,dt + \int_{E_x} f(t)\,dt.$$

Hence
$$\left| \int_G f(x+t)\,dt - \int_G f(t)\,dt \right| < 2e',$$

for all values of x numerically less than X.

This shows that, as x approaches zero, all possible limits of $\int_G f(x+t)\,dt$

* This theorem and that of the next article might have deduced from a theorem, to which my attention has been called, proved by Lebesgue on pp. 15 and 16 of his 'Leçons sur les Séries Trigonométriques.'

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differ from $\int_G f(t)\,dt$ by, at most, $2\epsilon'$, and therefore all coincide with $\int_G f(t)\,dt$, since ϵ' may be as small as we please. Thus, $\int_G f(x+t)\,dt$ is continuous with respect to x at $x = 0$.

Writing $a+x$ for x, the same argument proves that the integral is continuous at $x = a$. Hence the integral is a continuous function of x, as was to be proved.

§ 5. Theorem.—*If $f(t)$ is a summable function of t, and $g(t)$ is a bounded function,*

$$\int_a^b f(t+x)\,g(t)\,dt,$$

is a continuous function of x.

Case 1.—Let $f(t) \geq 0$.

Divide the whole range (K, K′) of values of $g(t)$ into n equal parts, and let $H_0, H_1, H_2, \ldots, H_n$, be the corresponding sets of points, so that, for instance, H_r is the set of points at which

$$K+r(K'-K)/n \leq g(t) < K+(r+1)(K'-K)/n. \qquad (1)$$

Also let $g_r(t)$ denote the function which is zero except at the points of H_r, and at the points of that set has as value the greatest of the three quantities given in the inequality (1). Then at the points of H_r the new function $g_r(t)$ differs from $g(t)$ by at most $(K'-K)/n$.

Now $$\int_a^b f(x+t)\,g_r(t)\,dt = [K+(r+1)(K'-K)/n]\int_{H_r} f(x+t)\,dt,$$

so that, by the preceding theorem, this integral is a continuous function of x. Hence also

$$\sum_0^n \int_a^b f(x+t)\,g_r(t)\,dt = F(x, n)$$

is a continuous function of x. Moreover, by what was already pointed out, it is greater than $\int_b^a f(x+t)\,g(t)\,dt$ by at most $(K'-K)\int_a^b f(x+t)\,dt/n$, that is by less than $(K'-K)M/n$, where M is a fixed quantity, since $\int_a^b f(x+t)\,dt$ is a continuous function of x, and has, therefore, finite upper and lower bounds. Hence, as n increases indefinitely, $F(x, n)$ converges uniformly to

$$\int_a^b f(x+t)\,g(t)\,dt$$

as unique limiting function, and therefore that limiting function is a continuous function of x.

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Case 2.—Let $f(t)$ be sometimes positive, sometimes negative.

Then $f(t)$ is the difference of two positive summable functions, one of which is equal to $f(t)$ except where $f(t)$ is negative, where the new function is zero. In this way our integral can be expressed as the difference of two integrals each of which is a continuous function of x, by Case 1, so that in this case also the integral is a continuous function of x.

Thus in every case the theorem is true.

Cor.—*If $g(t)$ is only bounded below (above), the integral in question is a lower (upper) semi-continuous function of x in the extended sense, the value infinity above (below) being admitted, provided $f(t)$ is positive, or bounded below.*

If $f(t)$ is negative, or bounded above, and $g(t)$ is bounded below (above), the integral is an upper (lower) semi-continuous function of x.

For, supposing $f(t)$ to be positive, and denoting by $g_k(t)$ the function equal to $g(t)$ wherever $g(t) \leq k$ and elsewhere zero, we know, by the definition of the integral that the integral in question is the unique limit when k increases indefinitely of the integral

$$\int_a^b f(x+t)\, g_k(t)\, dt.$$

This latter integral is, by the above theorem, a continuous function of x, and it is a monotone increasing function of k, so that the limiting function is a lower semi-continuous function of x. This proves the first of the alternative theorems; similarly the others may be proved.

§ 6. Theorem.—*If $f(t)$ and $g(t)$ are such that their squares are summable, then*

$$\int_b^a f(x+t)\, g(t)\, dt$$

is a continuous function of x.

Let Q denote the content of the set of those points at which $g(t)$ is numerically greater than k. Then, since the square of $g(t)$ is summable, we can choose k so large that

$$\int_Q [g(t)]^2\, dt \leq e,$$

where e is any chosen positive quantity.

But, since the squares of $f(t)$ and $g(t)$ are summable, we have, by Schwarz's inequality,

$$\left[\int_Q f(t+x)\, g(t)\, dt\right]^2 \leq \int_Q [f(t+x)]^2\, dt \int_Q [g(t)]^2\, dt$$

$$\leq e \int_Q [f(t+x)]^2\, dt$$

$$\leq eM,$$

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where M is the upper bound of the continuous function of x represented by $\int_Q [f(t+x)]^2\,dt$.

Hence

$$\int_a^b f(x+t)\,g(t)\,dt = \int_a^b f(x+t)\,g_k(t)\,dt + \int_Q f(t+x)\,g(t)\,dt$$
$$= G(x,k) + \sqrt{e'M},$$

where $g_k(t) = g(t)$, wherever it is numerically $\leq k$, and elsewhere $g_k(t) = 0$, so that, by the preceding theorem, $G(x,k)$ is a continuous function of x, and e' is numerically $\leq e$.

This shows that $G(x,k)$ converges uniformly to the integral on the left, which is therefore a continuous function of x.

§ 7. The preceding theorem is a special case of the following, in which p represents any positive quantity (not zero), rational or irrational.

Theorem.—*If $f(t)$ and $g(t)$ are such that $[f(t)]^{1+p}$ and $[g(t)]^{1+1/p}$ are summable, then*

$$\int_a^b f(x+t)\,g(t)\,dt$$

is a continuous function of x.

For since the arithmetic mean is not less than the geometric mean, we have, for all positive integers r and s,

$$(u^r v^s)^{1/(r+s)} \leq (ru+sv)/(r+s).$$

Putting $u = U^{(r+s)/r}$, $v = V^{(r+s)/s}$, $sp = r$, this gives

$$(1+p)\,UV \leq pU^{1+1/p} + V^{1+p}. \qquad (1)$$

Since this is true for every positive rational value of p, it is also true for every positive irrational value of p.

Hence, if $f(t)$ and $g(t)$ are positive functions,

$$(1+p)f(x+t)\,g(t) \leq p\,[g(t)]^{1+1/p} + [f(x+t)]^{1+p}.$$

Integrating over any set Q,

$$(1+p)\int_Q f(x+t)\,g(t)\,dt \leq p\int_Q [g(t)]^{1+1/p}\,dt + \int_Q [f(x+t)]^{1+p}\,dt$$
$$\leq p\int_Q [g(t)]^{1+1/p}\,dt + \int_{Q_x} [f(t)]^{1+p}\,dt, \qquad (2)$$

where Q_x is the set got from Q by translation through a distance x.

Now let Q denote the set of those points at which $[g(t)]^{1+1/p}$ is numerically greater than k, where k is chosen so large that the content of Q is less than an assigned small positive quantity e'; this is possible, since $[g(t)]^{1+1/p}$ is summable.

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Moreover, by the fundamental property of an integral, e' could be chosen so small that the integrals of $[g(t)]^{1+1/p}$ and $[f(t)]^{1+p}$ over any set of content less than e' are less than e, where e is a small positive quantity chosen previous to all.

In this way, since Q_x has the same content as Q, each of the integrals on the right-hand side of (2) is numerically less than e. Thus

$$(1+p)\int_Q f(x+t)\,g(t)\,dt \leq (p+1)\,e.$$

Hence

$$\int_a^b f(x+t)\,g(t)\,dt = \int_a^b f(x+t)\,g_k(t)\,dt + \int_Q f(x+t)\,g(t)\,dt = G(x,k)+e''.$$

where e'' is $\leq e$ and $G(x, k)$ is a continuous function of x, since $g_k(t)$ denotes the function $= g(t)$ wherever it is $\leq k$, and $g(t)$ is zero elsewhere. Hence, $G(x, k)$ converges uniformly as k increases indefinitely to the integral under consideration, which is therefore a continuous function of x.

This proves the theorem in the case when $f(t)$ and $g(t)$ are positive functions. Hence, changing the sign of either or both the functions, it at once follows that the theorem is true, provided $f(t)$ and $g(t)$ retain their sign. But in the general case we have only to split up f into f_1+f_2 and g into g_1+g_2 in the usual way, where f_1 and g_1 are positive and f_2 and g_2 are negative, to express our integral as the sum of four integrals, each of which has already been proved continuous. Thus in the general case also the integral under consideration is a continuous function of x, which proves the theorem.

§ 8. Theorem.—*If $f(t)$ is summable and $g(t)$ is bounded, we may reverse the order of repeated integration and write*

$$\int_a^b dx \int_c^d f(x+t)\,g(t)\,dt = \int_c^d dt \int_a^b f(x+t)\,g(t)\,dx.$$

First let f be a positive function.

Then since the repeated integrals of $f(x+t)$ evidently exist and are equal, we may, by a known theorem,* reverse the order of integration.

Next let f be not always positive.

Then we can write

$$f(t) = f_1(t) - f_2(t),$$

where f_1 and f_2 are both positive functions, f_1 being equal to f wherever $f = 0$, and being zero elsewhere. Expressing our integral as the difference of two integrals, one involving f_1 and the other f_2, the required result follows,

* W. H. Young, "On Change of Order of Integration in an Improper Repeated Integral," 'Camb. Phil. Soc. Trans.,' 1910, vol. 21, p. 364.

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since, by what has been already remarked, we may reverse the order of integration in each of the two auxiliary integrals.

§ 9. Theorem.—*If* $f(t)$ *and* $g(t)$ *are such that* $[f(t)]^{1+p}$ *and* $[g(t)]^{1+1/p}$ *are summable, then we may reverse the order of repeated integration, and write*

$$\int_a^b dx \int_c^d f(x+t)\, g(t)\, dt = \int_c^d dt \int_a^b f(x+t)\, g(t)\, dx.$$

As in the proof of the theorem of § 7,

$$\int_a^b f(x+t)\, g(t)\, dt = \int_a^b f(x+t)\, g_k(t)\, dt + e'', \tag{1}$$

where $e'' < e$, and g_k is a bounded function of t, having $g(t)$ as limit when k increases indefinitely. Since, by the theorem quoted, the left-hand side of this equation is a continuous function of x, and the same is true of the integral on the right, while e'' is bounded, we may integrate with respect to x, and get

$$\int_c^d dx \int_a^b f(x+t)\, g(t)\, dt = \int_c^d dx \int_a^b f(x+t)\, g_k(t)\, dt + \int_c^d e''\, dx.$$

Now $g_k(t)$ is a bounded function, therefore, by the preceding theorem, we may reverse the order of integration in the first integral on the right in the preceding equation. We thus get

$$\left| \int_c^d dx \int_a^b f(x+t)\, g(t)\, dt - \int_a^b dt \int_c^d f(x+t)\, g_k(t)\, dt \right| < e(d-c). \tag{2}$$

Letting e diminish down to zero as limit, k increases without limit, so that by de la Vallée Poussin's definition of an improper integral, $\int_c^d f(x+t)\, g_k(t)\, dt$ has as limit $\int_c^d f(x+t)\, g(t)\, dt$. Thus, by (2) we get in the limit

$$\int_c^d dx \int_a^b f(x+t)\, g(t)\, dt - \int_a^b dt \int_c^d f(x+t)\, g(t)\, dt = 0.$$

This proves the theorem.

Cor.—*The theorems of* §§ 8, 9, *remain true if we introduce into the integrand any bounded factor* $h(x, t)$.

For, in the first place, if $f(t)$ and $g(t)$ are positive functions, the corollary is an immediate consequence of the known theorem already quoted. If $f(t)$ and $g(t)$ are not positive functions, we may write $f = f_1 - f_2$, and $g = g_1 - g_2$, where f_1, f_2, g_1 and g_2 are positive functions, while f_1 and f_2 both enjoy the same property as to summability as f, and g_1 and g_2 as g. Thus the corollary holds when the integrand is any one of the four products

$$f_i(x+t)\, g_j(t)\, h(x, t),$$

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i and j being either 1 or 2. By suitable additions and subtractions it at once follows that the corollary is true.

§ 10. In the following theorems the functions f and g are supposed to be summable, and we consider their Fourier series. In the integrals between the limits of integration $(-\pi, \pi)$ which occur, f and g are supposed to be rendered periodic in the usual way, by attributing outside the interval $(-\pi, \pi)$ the values in that interval periodically. The properties of f and g hypothecated as to boundedness or summability are, of course, unaffected by this convention. We now have, however, by a simple change of variable,

$$\int_{-\pi}^{\pi} f(x+t)\,g(t)\,dt = \int_{-\pi+x}^{\pi+x} f(t)\,g(t-x)\,du = \int_{-\pi}^{\pi} f(t)\,g(t-x)\,dt,$$

$$\int_{-\pi}^{\pi} f(t-x)\,g(t)\,dt = \int_{-\pi-x}^{\pi-x} f(t)\,g(t+x)\,du = \int_{-\pi}^{\pi} f(t)\,g(t+x)\,dt,$$

so that

$$\int_{-\pi}^{\pi} [f(t+x) \pm f(t-x)]\,g(t)\,dt = \pm \int_{-\pi}^{\pi} [g(t+x) \pm g(t-x)]\,f(t)\,dt. \quad \text{(A)}$$

Thus, for instance, in applying the preceding theorems, the hypotheses with respect to f and g may be interchanged without affecting the result.

It should also be remarked that, owing to the periodicity of the functions which occur in the integrands, the functions denoted by the integrals are themselves periodic, so that at the extremities of the interval $(-\pi, \pi)$ their values agree. Thus the continuity of the integrals at these extremities has the special character so often required in the applications to Fourier series.

§ 11. Theorem.—*If $f(t)$ and $g(t)$ are such that $[f(t)]^{1+p}$ and $[g(t)]^{1+1/p}$ are summable, or if $f(t)$ is summable and $g(t)$ bounded, and if the Fourier series of f and g are*

$$f(t) \sim \tfrac{1}{2}a_0 + \sum_{n=1} (a_n \cos nt + b_n \sin nt)$$

$$g(t) \sim \tfrac{1}{2}\alpha_0 + \sum_{n=1} (\alpha_n \cos nt + \beta_n \sin nt),$$

then

$$\tfrac{1}{2}a_0\alpha_0 + \sum_{n=1} (a_n\alpha_n + b_n\beta_n) \cos nt$$

is a Fourier series and the corresponding function is

$$\frac{1}{2\pi}\int_{-\pi}^{\pi} [f(t+x)+f(t-x)]\,g(t)\,dt.^*$$

For, in either of the cases specified, we can, as we have seen (§§ 8, 9), reverse the order of integration in the repeated integral

$$\int_a^b dt \int_c^d f(t+x)\,g(t) \cos nx\,dx.$$

* In this integral f and g must be supposed to have been made periodic in the usual way, see § 10.

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Hence, denoting the function given at the end of the enunciation by $q(x)$,

$$\frac{1}{\pi}\int_{-\pi}^{\pi} q(x)\cos nx\,dx = \frac{1}{2\pi^2}\int_{-\pi}^{\pi}dt\int_{-\pi}^{\pi} f(t+x)\,g(t)\cos nx\,dx$$
$$+\frac{1}{2\pi^2}\int_{-\pi}^{\pi}dt\int_{-\pi}^{\pi} f(t-x)\,g(t)\cos nx\,dx$$
$$=\frac{1}{2\pi^2}\int_{-\pi}^{\pi}dt\int_{-\pi}^{\pi} f(u)\,g(t)\cos n(u-t)\,du$$
$$+\frac{1}{2\pi^2}\int_{-\pi}^{\pi}dt\int_{-\pi}^{\pi} f(u)\,g(t)\cos n(t-u)\,du,$$

where, in the changes of variable here used, the limits of integration may still be taken to be $-\pi$ and π, by reason of the periodicity of the integrands. Hence the integral on the left

$$=\frac{1}{\pi}\int_{-\pi}^{\pi} f(u)\cos nu\,du\,\frac{1}{\pi}\int_{-\pi}^{\pi} g(t)\cos nt\,dt+\frac{1}{\pi}\int_{-\pi}^{\pi} f(u)\sin nu\,du\,\frac{1}{\pi}\int_{-\pi}^{\pi} g(t)\sin nt\,dt$$
$$=a_n\alpha_n+b_n\beta_n.$$

Since $\int_{-\pi}^{\pi} q(x)\sin nx\,dx$ is obviously zero, this proves the theorem.

Cor.—*The above theorem remains true in all cases in which the reversal of the order of partial differentiation used at the beginning of the proof is allowable.*

§ 12. Theorem.—*If $f(t)$ and $g(t)$ are such that $[f(t)]^{1+p}$ and $[g(t)]^{1+1/p}$ are summable, or if $f(t)$ is summable and $g(t)$ bounded, and if the Fourier constants of f are a_n, b_n, and those of g are α_n and β_n, then*

$$\sum_{n=0}(a_n\beta_n-b_n\alpha_n)\sin nx$$

is a Fourier series, and the corresponding function is

$$\frac{1}{2\pi}\int_{-\pi}^{\pi}[f(t+x)-f(t-x)]\,g(t)\,dt.$$

The proof is on precisely the same lines as that of the last theorem. We merely have to interpret $q(x)$ as the function just given, and replace the cosines by sines, and we get

$$\frac{1}{\pi}\int_{-\pi}^{\pi} q(x)\sin nx\,dx = a_n\beta_n-b_n\alpha_n.$$

Since $\int_{-\pi}^{\pi} q(x)\cos nx = 0$, this proves the theorem.

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§ 13. Theorem.—*If*

$$f(t) \backsim \tfrac{1}{2}a_0 + \sum_{n=1} (a_n \cos nt + b_n \sin nt), \tag{1}$$

and

$$g(t) \backsim \tfrac{1}{2}\alpha_0 + \sum_{n=1} (\alpha_n \cos nt + \beta_n \sin nt), \tag{2}$$

then

$$\frac{1}{\pi}\int_{-\pi}^{\pi} [f(t+x)+f(t-x)]\, g(t)\, dt = \tfrac{1}{2}a_0\alpha_0 + \sum_{n=1} (a_n\alpha_n + b_n\beta_n) \cos nx, \tag{3}$$

and

$$\frac{1}{\pi}\int_{-\pi}^{\pi} [f(t+x)-f(t-x)]\, g(t)\, dt = \sum_{n=1} (a_n\beta_n - b_n\alpha_n) \sin nx, \tag{4}$$

for all values of x in each of the two following cases:—

(i) *$f(t)$ is summable and $g(t)$ a function of bounded variation;*

(ii) *the squares of $f(t)$ and $g(t)$ are summable functions;*

and for every value of x for which the last series has a unique limit (sum), when $[f(t)]^{1+p}$ and $[g(t)]^{1+1/p}$ are summable functions.

For in all these cases, as has been proved, the series (3) and (4) are Fourier series, and the integrals on the left are the corresponding Fourier functions, so that the statements (3) and (4) are true if we replace the sign = by $\backsim$.

But the integrals on the left of (3) and (4) have been shown to be continuous functions of x in all the cases here considered. Hence, by a known property of Fourier series, the series (3) and (4) cannot diverge properly, and they represent their Fourier functions, except at points where they oscillate. This proves the final statement. It remains to prove that, in cases (i) and (ii), the series (3) and (4) do not oscillate.

In case (i) we use the equality (A) of § 10

$$\int_{-\pi}^{\pi} [f(t+x) \pm f(t-x)]\, g(t)\, dt = \pm \int_{-\pi}^{\pi} [g(t+x) \pm g(t-x)]\, f(t)\, dt, \tag{A}$$

to show that each of these functions of x has bounded variation. For the property of being monotone is obviously preserved in parametric integration. Hence, the integrand of the second of the integrals in (A) being in our case a function of x of bounded variation, that integral, and therefore also the other integral, represents a function of x of bounded variation.

But the Fourier series of a function of bounded variation always represents that function. This, therefore, proves the theorem in case (i).

In case (ii) both $[f(t)]^2$ and $[g(t)]^2$ are summable, therefore, putting $p = 1$, $x = 0$, in the result already proved in our final case, and, taking f and g to be the same, we have

$$\frac{1}{\pi}\int_{-\pi}^{\pi} [f(t)]^2\, dt = \tfrac{1}{2}a_0^2 + \sum_{n=1} (a_n^2 + b_n^2), \tag{5}$$

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where we have introduced the sign of equality, since the series on the right, being a series of positive terms, cannot oscillate.

Similarly
$$\frac{1}{\pi}\int_{-\pi}^{\pi}[g(t)]^2\,dt = \tfrac{1}{2}\alpha_0^2 + \sum_{n=1}(\alpha_n^2+\beta_n^2), \qquad (6)$$

Hence the series (3) and (4) converge for all values of x, since each of the terms is numerically less than, or equal to, the sum of the corresponding terms of the convergent series (5) and (6). Thus, by what was already proved for our final case, the theorem holds in case (ii).

Thus the complete theorem is proved.

Cor. 1.—*In cases* (i) *and* (ii) *the convergence of the series* (3) *is uniform.*

For the Fourier series of a continuous function of bounded variation converges uniformly, while in the above proof, in case (ii), the test for the convergence is Weierstrass's test for uniform convergence.

Cor. 2.—*In the final case of the preceding theorem, the equalities* (3) *and* (4) *hold for all values of x, provided the summation of the series be performed in the Cesaro manner, and the series converge then uniformly.*

For a Fourier series converges, and converges uniformly, at every point at which the function is continuous, when summed in the Cesaro way.

§ 14. In the preceding article only a few of the consequences of the fact that the trigonometrical series whose general terms are respectively

$$(a_n\alpha_n+b_n\beta_n)\cos nx \quad \text{and} \quad (a_n\beta_n-b_n\alpha_n)\sin nx$$

are, under the various circumstances specified in § 13, the Fourier series of continuous functions have been deduced. For the purposes of application the mere fact that these series are Fourier series will often suffice, quite irrespective of whether they converge or not. Moreover, from the fact that the functions to which they belong are continuous it follows that their allied series, viz., those whose general terms are

$$(a_n\alpha_n+b_n\beta_n)\sin nx \quad \text{and} \quad (a_n\beta_n-b_n\alpha_n)\cos nx$$

are Fourier series.

In fact, if we denote for brevity the functions of which the two series first mentioned are the Fourier series by $q_1(x)$ and $q_2(x)$, then the two latter series have for their Fourier functions

$$\frac{1}{\pi}\frac{d}{dx}\int_0^{\pi}[q_1(x+t)+q_1(x-t)]\log\tfrac{1}{2}\operatorname{cosec}\tfrac{1}{2}t\,dt$$

and
$$\frac{1}{\pi}\frac{d}{dx}\int_0^{\pi}[q_2(x+t)+q_2(x-t)]\log\tfrac{1}{2}\operatorname{cosec}\tfrac{1}{2}t\,dt$$

respectively.

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This is, indeed, an immediate consequence of the formula (IV) on p. 19 of my recent paper "On the Fourier Constants of a Function."*

§ 15. In certain cases these two new functions are also plainly continuous. A knowledge, however, of $q_1(x)$ and $q_2(x)$ alone will often suffice to determine the question of the convergence of the allied series, as well as of the series to which they themselves belong. It follows, in fact, from § 10 of the paper just quoted,† and other known results, that if $q_1(x)$, for example, has all its derivates finite, not necessarily bounded, then both the series to which it belongs and the allied series will converge everywhere; they will, moreover, converge at an isolated point at which all the four derivates are finite.

We may sum up all these and other facts of a similar nature by saying that the whole question as to the convergence, or other properties, of the four series, whether for all values, or for particular values, of the variable x, is reducible to a discussion of the properties of certain parametric integrals. Moreover, sufficient indications have been given as to the properties of these integrals in a large and important class of cases.

§ 16. *Added May* 15.—So far we have only considered ordinary Fourier series. The method of the paper may, however, be applied to generalised Fourier series. We may thus, for example, obtain a second proof of the theorem of § 9 of my paper quoted in § 1.

It should also be remarked that the whole question of the convergence of the series $\Sigma(a_n\alpha_n+b_n\beta_n)$ and $\Sigma(a_n\beta_n-b_n\alpha_n)$ in the most general case in which the coefficients refer to ordinary Fourier series may be shown to turn on the properties of the functions

$$\frac{d}{dx}\left\{\frac{1}{\pi}\int_{-\pi}^{\pi}[\mathrm{F}(t+x)-\mathrm{F}(t-x)]\,g(t)\,dt\right\}$$

and

$$\frac{d}{dx}\left\{\frac{1}{\pi}\int_{-\pi}^{\pi}[\mathrm{F}(t+x)+\mathrm{F}(t-x)]\,g(t)\,dt\right\}.$$

The Fourier series of these functions, which may be proved to exist except for a set of values of x of content zero, are easily seen to be $\Sigma(a_n\alpha_n+b_n\beta_n)\cos nx$ and $\Sigma(a_n\beta_n-b_n\alpha_n)\sin nx$. Here $f(t)$ and $g(t)$ may be any summable functions, and $\mathrm{F}(t)$ denotes $\int_0^t f(t)\,dt$.

* 'Roy. Soc. Proc.,' 1911, A, vol. 85, pp. 14—24. In this formula IV on p. 19, as well as in the last five formulæ on p. 21, the factor $1/\pi$ has been omitted on the left-hand side.

† It may be noted that the result in question may also be obtained by actual summation of the first n terms of the allied series, and the use of a theorem of Riemann-Lebesgue.

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On a Mode of Generating Fourier Series.

By W. H. Young, Sc.D., F.R.S.

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§ 1. In a recent paper* published in the 'Proceedings' of this Society I obtained formulæ for the sum of the series formed by the Fourier constants of a function, when each of these is divided by a power of the index giving its place in the series. As I there remarked, the scope of these results is really wider than at first appears, and I undertook to develop later their further consequences. The present communication is the outcome of this undertaking. I have, however, already in part indicated in a second still more recent paper† the general nature of the argument which I propose to employ.

I start with a Fourier series

$$f(x) \sim \sum_{n=1}^{\infty} (a_n \cos nx + b_n \sin nx),$$

and its allied series

$$\sum_{n=1}^{\infty} (-a_n \sin nx + b_n \cos nx).$$

I then substitute in both series $n^{-q}a_n$ for a_n and $n^{-q}b_n$ for b_n. The series thus generated are shown to be both Fourier series, whatever positive value be attributed to q, and this whether the allied series be a series of Fourier or not. Let us denote the Fourier functions of the new series by $g(x)$ and $h(x)$. Then it appears that if $f(x)$ is bounded, $g(x)$ and $h(x)$ are necessarily continuous. If, instead of being bounded, $f(x)$ has its $(1+p)$th power summable, p being any positive quantity, then $g(x)$ and $h(x)$ are still continuous, provided $q > 1/(p+1)$. From this it follows, in particular, that when $f(x)$ has its $(1+p)$th power summable, and $q > 1/(1+p)$, the series whose general terms are $n^{-q}a_n$ and $n^{-q}b_n$ cannot diverge properly and that when summed in the Cesaro way they have for sums the expressions given on p. 18 of the first paper above cited. Further, the series $\sum_{n=1}^{\infty} n^{-q}(a_n^2 + b_n^2)$ necessarily converges, however small p may be, and its sum can be written down.

If $f(x)$ is a function, necessarily continuous, satisfying the generalised

* "On the Fourier Constants of a Function," 'Roy. Soc. Proc.,' A, 1911, vol. 85, pp. 14—24.

† See preceding paper.

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condition of Lipschitz, which requires that for each positive value of δ less than a fixed positive quantity d, less than unity,

$$\frac{f(x)-f(y)}{(x-y)^\delta}$$

should be bounded, then these functions $g(x)$ and $h(x)$ are integrals, provided only that $q>1-d$. This leads at once to the further conclusion that if we substitute $n^q a_n$ for a_n and $n^q b_n$ for b_n, in other words, if we employ the reverse process to that previously described, we still get series of Fourier, provided only $q<d$. We are thus able, in particular, to assert that $n^q a_n$ and $n^q b_n$ have in the case of a function satisfying such a generalised condition of Lipschitz the unique limit zero as n increases indefinitely, provided $q<d$, a conclusion which agrees with Lebesgue's* recent investigations on the order of magnitude of the coefficients of such a Fourier series. But, further, it leads to the striking result that in this case also $\sum_{n=1}^{\infty} n^q (a_n^2+b_n^2)$ converges and that, more generally, if a'_n, b'_n, refer to another function of the type considered in which d' takes the place of d, then the series whose general terms are respectively $n^q(a_n a'_n+b_n b'_n)$ and $n^q(a_n b'_n-a'_n b_n)$ necessarily converge, provided only that $2q<d+d'$. Moreover, simple expressions are found for the sums of these series.

If $f(x)$ is a function of bounded variation, then however small q may be taken, the direct process always leads to functions $g(x)$ and $h(x)$ which are integrals. From this it follows that the reverse process performed on the Fourier series of a function of bounded variation and on the allied series always lead to Fourier series, provided q is less than unity. This includes, of course, the known result that in the case of such a series, $n^q a_n$ and $n^q b_n$ have the unique limit zero when q is less than unity. It also enables us to write down the sum of $\sum_{n=1}^{\infty} n^q (a_n^2+b_n^2)$, $q<1$, and a number of similar expressions.

The essential features of the investigations consist, in fact, in the actual formation and discussion of expressions for $g(x)$ and $h(x)$. It seems therefore not unlikely that closer scrutiny of these expressions may lead to the discovery of further properties. That we cannot pass, however, by the process described, when $q<1$, from the general continuous function even to a function of bounded variation, however near q be taken to unity, appears from the mere inspection of Weierstrass's non-differentiable function. It is

* H. Lebesgue, "Sur la représentation trigonométrique approchée des fonctions satisfaisant à une condition de Lipschitz," 'Bull. de la Soc. Math. de France,' 1910, vol. 38 pp. 1—27.

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probable therefore that the statements just made are, as far as they go, and in their general outline, complete.

§ 2. We shall require the following theorem in parametric integration :—

Theorem.—*If* $\mathrm{F}(t)$ *is an integral and* $g(t)$ *is a summable function in the interval* (a, b), $\int_a^b \mathrm{F}(x \pm t)\, g(t)\, dt$ *is, when regarded as a function of* x, *an integral.*

For by the fundamental property of an integral, as formulated by Vitali,* we can fix e and then find E, so that, provided only

$$\Sigma h_n < \mathrm{E},$$

we have

$$\Sigma |\mathrm{F}(\mathrm{X}_n + h_n) - \mathrm{F}(\mathrm{X}_n)| < e;$$

here the left-hand side of the preceding inequality represents the total increment of $\mathrm{F}(x)$ over the set of intervals $(\mathrm{X}_n, \mathrm{X}_n + h_n)$, supposed to be non-overlapping.

This being true for all positions of the points X_n which permit the intervals to be constructed in accordance with these conditions, it is true when we translate each interval the same distance t in the same direction, that is, it is true when for X_n we write $\mathrm{X}_n + t$. Hence for the same system of quantities h_n, we have, denoting $\int_a^b \mathrm{F}(x+t)\, g(t)\, dt$ by $\mathrm{K}(x)$,

$$\Sigma |\mathrm{K}(\mathrm{X}_n + h_n) - \mathrm{K}(\mathrm{X}_n)| < e \int_a^b |g(t)|\, dt,$$

which, by Vitali's condition, shows that $\mathrm{K}(x)$ is an integral.

§ 3. We are now able to prove the following fundamental result :—

Theorem.—*If* $\sum_{n=1}^{\infty} (a_n \cos nx + b_n \sin nx)$ *is a Fourier series,*† *so are*

$$\sum_{n=1}^{\infty} n^{-q} (a_n \cos nx + b_n \sin nx) \quad \textit{and} \quad \sum_{n=1}^{\infty} n^{-q} (-a_n \sin nx + b_n \cos nx),\ 0 < q.$$

Moreover, the Fourier functions of these latter series are expressible in a simple manner in terms of that of the former series.

First, let $q < 1$ and suppose

$$f(x) \backsim \sum_{n=1}^{\infty} (a_n \cos nt + b_n \sin nt),$$

* G. Vitali, "Sulle funzioni integrali," 'Atti di Torino,' 1905, vol. 40, pp. 1021—1034. See also my paper on "Semi-integrals and Oscillating Successions of Functions," 'Lond. Math. Soc. Proc.,' 1910, Series II, vol. 9, pp. 286—324.

† There is no loss of generality in assuming, as we do here, that the constant term is absent. See W. H. Young, "On the Conditions that a Trigonometrical Series should have the Fourier Form," 'Lond. Math. Soc. Proc.,' 1910, Series II, vol. 9, pp. 421—433.

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so that $$F(t) = \int_0^t f(t)\,dt = \tfrac{1}{2}K + \sum_{n=1}^{\infty} (a_n \sin nt - b_n \cos nt)/n,$$

where K is a constant, and therefore

$$F(x+t)+F(x-t) = K + 2\sum_{n=1}^{\infty} n^{-1}(a_n \sin nx - b_n \cos nx)\cos nt.$$

Since F is an integral, and therefore a function of bounded variation, and $q<1$, we may now use formula (I), on p. 18 of my paper on "The Fourier Constants of a Function,"* and thus get

$$\int_0^{\infty} t^{q-1}[F(x+t)+F(x-t)-K]\,dt = C\sum_{n=1}^{\infty} n^{-1-q}(a_n \sin nx - b_n \cos nx), \quad (1)$$

where $$C = 2\cos \tfrac{1}{2}q\pi\,\Gamma(q).$$

Now $\int_0^1 t^{q-1}F(x \pm t)\,dt$ is an integral when regarded as a function of x, by the theorem of § 2.

Also, since

$$F(x+t)+F(x-t)-F(t)-F(-t)+F(t)+F(-t)-K$$
$$= \int_0^x [f(u+t)+f(u-t)]\,du + F(t)+F(-t)-K,$$

$$\int_1^p t^{q-1}[F(x+t)+F(x-t)-K]\,dt$$
$$= \int_1^p dt \int_0^x t^{q-1}[f(u+t)+f(u-t)]\,du + \int_1^p t^{q-1}[F(t)+F(-t)-K]\,dt$$
$$= \int_0^x du \int_1^p [f(u+t)+f(u-t)]\,t^{q-1}dt + \int_1^p t^{q-1}[F(t)+F(-t)-K]\,dt,$$

where we have in the repeated integral changed the order of integration, since $f(t)$ is summable and t^{q-1} is bounded.†

Using the Second Theorem of the Mean, the inner integral of this latter repeated integral may be written

$$\int_1^P [f(u+t)+f(u-t)]\,dt = F(u+P)+F(u-P)-F(u+1)-F(u-1),$$

and therefore traces out a bounded sequence as p moves off to infinity, since F is periodic, and $\int_1^{\infty} t^{q-1}[F(x+t)+F(x-t)-K]\,dt$ exists, both when x is zero and when it is not.

Hence

$$\operatorname*{Lt}_{p=\infty} \int_0^x du \int_1^p [f(u+t)+f(u-t)]\,t^{q-1}\,dt = \int_0^x du \int_1^{\infty} [f(u+t)+f(u-t)]\,t^{q-1}\,dt,$$

* *Loc. cit.*

† *Loc. cit.*, "On a Class of Parametric Integrals," § 9.

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and therefore

$$\int_1^\infty t^{q-1}[\mathrm{F}(x+t)+\mathrm{F}(x-t)-\mathrm{K}]\,dt = \int_0^x du \int_1^\infty [f(u+t)+f(u-t)]\,t^{q-1}\,dt + \int_1^\infty t^{q-1}[\mathrm{F}(t)+\mathrm{F}(-t)-\mathrm{K}]\,dt.$$

Thus our integral between the limits of integration $(1, \infty)$ is, when regarded as a function of x, an integral. Since the same has been shown to be true between the limits $(0, 1)$, it follows that it is true between the limits $(0, \infty)$, which proves that the series (1) converges to an integral, and therefore that the series

$$\sum_{n=1}^{\infty} n^{-q}(a_n \cos nx + b_n \sin nx)$$

is a Fourier series.

A precisely similar argument shows that the series

$$\sum_{n=1}^{\infty} n^{-q}(b_n \cos nx - a_n \sin nx)$$

is a Fourier series.

We have in fact

$$\mathrm{F}(x+t)-\mathrm{F}(x-t) = 2\sum_{n=1}^{\infty} n^{-1}(a_n \cos nx + b_n \sin nx)\sin nt.$$

We thus get, as before,

$$\int_0^\infty t^{q-1}[\mathrm{F}(x+t)-\mathrm{F}(x-t)]\,dt = \mathrm{C}'\sum_{n=1}^{\infty} n^{-1-q}(a_n \cos nx + b_n \sin nx),$$

where $$\mathrm{C}' = 2\sin \tfrac{1}{2}q\pi\,\Gamma(q);$$

and it is evident that the rest of the argument is the same as before. If q is not less than unity, it is clear that, by repeating the argument, the same result holds good.

Cor.—*Thus, with the notation of the theorem, we have, if* $0 < q < 1$,

$$\frac{d}{dx}\int_0^\infty t^{q-1}[\mathrm{F}(x+t)+\mathrm{F}(x-t)]-\frac{1}{\pi}\int_0^\pi [\mathrm{F}(t)+\mathrm{F}(-t)]\,dt \sim 2\cos \tfrac{1}{2}q\pi\,\Gamma(q)\sum_{n=1}^{\infty} n^{-q}(a_n \sin nx + b_n \sin nx)$$

and

$$\frac{d}{dx}\int_0^\infty t^{q-1}[\mathrm{F}(x+t)-\mathrm{F}(x-t)]\,dt \sim 2\sin \tfrac{1}{2}q\pi\,\Gamma(q)\sum_{n=1}^{\infty} n^{-q}(-a_n \sin nx + b_n \cos nx),$$

it being understood that, where the differential coefficients do not exist—which can only be the case for a set of values of x of content zero—the value zero, or any other convenient value, is assigned to the left-hand sides. The corresponding formulæ when $q \geq 1$ can easily be written down, using the formulæ on p. 22 instead of those on p. 18 of the Fourier constants paper.

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§ 4. So far $f(x)$ has been any summable function. We now suppose it to be subject to some further restrictions.

First let us suppose that, for some fixed positive quantity p, not necessarily rational, the $(1+p)$th power of $f(x)$ is summable. We can then at once get additional information if we restrict q to be greater than $1/(1+p)$. Moreover, the expressions just obtained for the Fourier functions take a still simpler form. We have in fact the following theorem :—

Theorem.—*If $f(x)$ has its $(1+p)$th power summable, and q is any quantity less than unity and greater than $1/(1+p)$, then*

$$\int_0^\infty [f(x+t)+f(x-t)]\, t^{q-1}dt \sim 2\cos \tfrac{1}{2}q\pi\Gamma(q) \sum_{n=1}^{\infty} n^{-q}(a_n \cos nx + b_n \sin nx)$$

and

$$\int_0^\infty [f(x+t)-f(x-t)]\, t^{q-1}dt \sim 2\sin \tfrac{1}{2}q\pi\Gamma(q) \sum_{n=1}^{\infty} n^{-q}(-a_n \sin nx + b_n \cos nx).$$

As before, the formulæ when $q \geq 1$ can easily be written down.

It will be sufficient to prove the former of these statements, as the argument in the two cases is identical. It depends first on the fact that, when we have expressed F as an integral, change of order of integration can be shown to be allowable in the repeated integral thus obtained.

Thus $$\int_0^1 t^{q-1}\mathrm{F}(x+t)\,dt = \int_0^1 dt \int_0^x t^{q-1} f(u+t)\,du + \int_0^1 t^{q-1}\mathrm{F}(t)\,dt.$$

Now $[f(u+t)]^{1+p}$ is summable, and $(t^{q-1})^{1+1/p}$ is also summable, since $q > 1/(1+p)$; hence we may by a theorem I have proved in a recent paper,* change the order of integration in the repeated integral on the right-hand side, and so get

$$\int_0^1 t^{q-1}\mathrm{F}(x+t)\,dt = \int_0^x du \int_0^1 t^{q-1} f(u+t)\,dt + \int_0^1 t^{q-1}\mathrm{F}(t)\,dt.$$

Bearing in mind that, by another theorem of the same paper, the inside integral in the new repeated integral represents a continuous function of u, we have

$$\frac{d}{dx}\int_0^1 t^{q-1}\mathrm{F}(x+t)\,dt = \int_0^1 f(x+t)\,t^{q-1}dt.$$

Similarly, $$\frac{d}{dx}\int_0^1 t^{q-1}\mathrm{F}(x-t)\,dt = \int_0^1 f(x-t)\,t^{q-1}dt.$$

Again

$$\int_1^k t^{q-1}[\mathrm{F}(x+t)+\mathrm{F}(x-t)-\mathrm{F}(t)-\mathrm{F}(-t)]\,dt = \int_1^k dt \int_0^x t^{q-1}[f(u+t)+f(u-t)]\,dt.$$

* *Loc. cit.*, "On a Class of Parametric Integrals," § 10.

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Now t^{q-1} is bounded in the region of values here considered, and $f(t)$ is a summable function. Hence change of order of integration is allowable* in the repeated integral on the right-hand side. Thus we have

$$\int_1^\infty t^{q-1}[\mathrm{F}(x+t)+\mathrm{F}(x-t)-\mathrm{F}(t)-\mathrm{F}(-t)]\,dt$$
$$= \operatorname*{Lt}_{k=\infty}\int_0^x du\int_1^k t^{q-1}[f(u+t)+f(u-t)]\,dt$$
$$= \int_0^x du \operatorname*{Lt}_{k=\infty}\int_1^k t^{q-1}[f(u+t)+f(u-t)]\,dt,$$

where the last step taken is allowable, since the inside integral in the repeated integral on the right is, by the Second Theorem of the Mean, equal to

$$\int_1^k [f(u+t)+f(u-t)]\,dt \quad (1 \leq k_1 < k_0),$$

that is $$\mathrm{F}(u+k_1)+\mathrm{F}(u-k_1)-\mathrm{F}(u+1)-\mathrm{F}(u-1),$$

and therefore is numerically less than a certain finite quantity, independent of k, as is obvious from the fact that $\mathrm{F}(t)$ is periodic.†

Thus the succession of functions of u denoted by the inside integral for increasing values of k forms a bounded and therefore an integrable sequence. It is, moreover, a uniformly convergent sequence, so that the limiting function is continuous. Hence, finally,

$$\frac{d}{dx}\int_1^\infty t^{q-1}[\mathrm{F}(x+t)+\mathrm{F}(x-t)-\mathrm{K}]\,dt = \int_1^\infty t^{q-1}[f(x+t)+f(x-t)]\,dt.$$

Bearing in mind the corresponding result obtained when the limits of integration are 0 and 1, we at once have the required result.

Cor. 1.—*If for all positive values of p less than some positive quantity* P, $f(x)$ *has its* $(1+p)$*th power summable, and q is any quantity greater than* $1/(1+\mathrm{P})$, *then the results of the theorem still hold.*

For if q be such a quantity, we can find $p < \mathrm{P}$ such that

$$1/(1+\mathrm{P}) < 1/(1+p) < q,$$

so that the theorem applies.

Cor. 2.—*Under the circumstances stated in the enunciation of the theorem or the corollary, the Fourier functions of the series generated are continuous functions.*

This has been shown in the course of the proof.

* *Loc. cit., supra*, § 3.

† Here again $f(x)$ must be supposed if necessary so modified by the subtraction of a suitable constant, that its Fourier series is deficient of constant term.

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Cor. 3.—*Under the same circumstances we obtain formulæ for the sums of* $\sum_{n=1}^{\infty} n^{-q}a_n$ *and* $\sum_{n=1}^{\infty} n^{-q}b_n$, *whenever these series converge. Moreover, these series necessarily converge in the Cesaro manner, by Cor.* 2, *and we have*

$$\int_0^{\infty}[f(t)+f(-t)]\,t^{q-1}dt/2\cos\tfrac{1}{2}q\pi\,.\,\Gamma(q) = \text{Cesaro}\sum_{n=1}^{\infty} n^{-q}a_n,$$

$$\int_0^{\infty}[f(t)-f(-t)]\,t^{q-1}dt/2\sin\tfrac{1}{2}q\pi\,.\,\Gamma(q) = \text{Cesaro}\sum_{n=1}^{\infty} n^{-q}b_n.$$

§ 5. We next suppose $f(x)$ to be a bounded function. We then need to make no restriction on the positive quantity q, and can still prove the same result. Thus we have the following theorem:—

Theorem.—*If* $f(x)$ *is any bounded function and* q *is any positive quantity less than unity, then*

$$\int_0^{\infty}[f(x+t)+f(x-t)]\,t^{q-1}dt \sim 2\cos\tfrac{1}{2}q\pi\Gamma(q)\sum_{n=1}^{\infty} n^{-q}(a_n\cos nx+b_n\sin nx)$$

and

$$\int_0^{\infty}[f(x+t)-f(x-t)]\,t^{q-1}dt \sim 2\sin\tfrac{1}{2}q\pi\Gamma(q)\sum_{n=1}^{\infty} n^{-q}(-a_n\sin nx+b_n\cos nx).$$

As before, the formulæ when $q \geq 1$ *can easily be written down.*

The mode of proof is precisely the same as that adopted in the proof of the theorem of the preceding article. The sole difference is that, in the discussion of the change of order of integration of the repeated integral which there occurs, we make use, when the limits of integration are 0 and 1, of different theorems from those there utilised. These theorems correspond, however, precisely to their analogues.

Cor. 1.—*Under the same circumstances the series of the theorem are the Fourier series of continuous functions.*

This is shown in the course of the proof.

Cor. 2.—The formulæ for $\sum_{n=1}^{\infty} n^{-q}a_n$ and $\sum_{n=1}^{\infty} n^{-q}b_n$, when summed in the Cesaro way, have been already given in my paper on "Fourier Constants." They follow once more here.

§ 6. We have seen that the Fourier functions obtained in §§ 4 and 5 are continuous functions. If in § 5 the function f has bounded variation we can prove these continuous functions to be integrals. We shall, for this purpose, require a special case of the following result in parametric integration:—

Theorem.—*If* q *is positive and less than unity, and* $f(x)$ *is any summable*

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function whose integral oscillates boundedly as the upper limit of integration x increases without limit, then

$$\int_1^\infty f(x+t)\, t^{q-1}dt \quad \text{and} \quad \int_1^\infty f(x-t)\, t^{q-1}dt$$

*are, when regarded as functions of x, both integrals.**

Since $f(x)$ is summable and t^{q-1} is an integral, we may integrate by parts. Thus, since the integral $\mathrm{F}(x)$ oscillates boundedly, so that $\mathrm{F}(\mu+t)\,\mu^{q-1}$ vanishes when μ becomes infinite, we have

$$\begin{aligned}
&\int_1^\infty t^{q-1} f(x+t)\, dt \\
&\quad = -\mathrm{F}(x+1) + \operatorname*{Lt}_{\mu=\infty}(1-q)\int_1^\mu \mathrm{F}(x+t)\, t^{q-2}dt \\
&\quad = -\mathrm{F}(x+1) + \operatorname*{Lt}_{\mu=\infty}(1-q)\int_1^\mu \left\{\int_0^x f(u+t)\, du + \mathrm{F}(t)\right\} t^{q-2}dt \\
&\quad = -\mathrm{F}(x+1) + (1-q)\int_1^\infty \mathrm{F}(t)\, t^{q-2}dt + \operatorname*{Lt}_{\mu=\infty}(1-q)\int_1^\mu dt \int_0^x f(u+t)\, t^{q-2}du.
\end{aligned} \tag{1}$$

Here the second term on the right certainly exists and is a finite constant, since $\mathrm{F}(t)$ by hypothesis is bounded, and $\int_1^\infty t^{q-2}dt$ exists. We have, therefore, only to show that the third term on the right is an integral when regarded as a function of x.

Now since $f(t)$ is summable, and t^{q-2} is bounded in $(1, \infty)$, we may reverse the order of integration, by a theorem already quoted, and write

$$\int_1^\mu dt \int_0^x f(u+t)\, t^{q-2}du = \int_0^x du \int_1^\mu f(u+t)\, t^{q-2}dt. \tag{2}$$

By the Second Theorem of the Mean,

$$\int_1^\mu f(u+t)\, t^{q-2}dt = \int_1^{\mu_1} f(u+t)\, dt = \mathrm{F}(u+\mu_1) - \mathrm{F}(u),$$

where $0 < \mu_1 < \mu$. This is therefore a bounded function of (u, μ), so that we may integrate term by term and write

$$\operatorname*{Lt}_{\mu=\infty}\int_0^x du \int_1^\mu f(u+t)\, t^{q-2}dt = \int_0^x du \operatorname*{Lt}_{\mu=\infty}\int_1^\mu f(u+t)\, t^{q-2}dt. \tag{3}$$

By (2) and (3),

$$\int_1^\infty dt \int_0^x f(u+t)\, t^{q-2}du = \int_0^x du \int_1^\infty f(u+t)\, t^{q-2}dt,$$

* The function t^{q-1} may here be replaced by a function $g(t)$ of a more general type. It will be sufficient if $g(t)$ vanishes at infinity and has a monotone decreasing differential coefficient $g'(t)$ in the whole open infinite interval.

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which shows that the third term on the right of (1) is an integral; therefore the same is true of the left-hand side of (1), when regarded as a function of x.

This proves the theorem as far as $\int_1^\infty f(x+t)\, t^{q-1}dt$ is concerned.

Similarly it follows for $\int_1^\infty f(x-t)\, t^{q-1}dt$.

§ 7. We shall next suppose $f(x)$ to be of bounded variation. We then have the following theorem :—

Theorem.—*If $f(x)$ has bounded variation, and q be a positive quantity less than unity, then $\int_0^1 t^{q-1}f(x+t)\,dt$ is, when regarded as a function of x, an integral.*

Since $f(t)$ has bounded variation, we may write

$$f(x+t) = \mathrm{P}(x+t) - \mathrm{N}(x+t),$$

where $\mathrm{P}(t)$ and $\mathrm{N}(t)$ are monotone increasing functions of t. Now

$$\int_e^1 t^{q-1}\mathrm{P}(x+t)\,dt = \left[t^{q-1}\int \mathrm{P}(x+t)\,dt\right]_e^1 - (q-1)\int_e^1 t^{q-2}\left\{\int \mathrm{P}(x+t)\,dt\right\}dt$$

is, since P is monotone, itself a monotone increasing function of x. Moreover, the integration by parts shows it to be an integral, when regarded as a function of x, by § 2. Thus, as e decreases, we get a monotone increasing sequence of functions of x, each of which functions is an integral, and is further increased at each stage by a monotone increasing function. We have, in fact, what I have called elsewhere* an ultra-monotone sequence of integrals. It at once follows that the limiting function is itself an integral.†

Substituting N for P, and subtracting our results, this proves that the integral considered is a function of x, which is an integral.

Thus our theorem is true.

Cor.—*If, in addition, the integral of $f(x)$ oscillates boundedly as x goes off to infinity, then $\int_0^\infty t^{q-1}f(x+t)\,dt$ is, when regarded as a function of x, an integral.*

In fact, by § 6, $\int_1^\infty t^{q-1}f(x+t)\,dt$ is an integral; hence, by addition, the required result follows.

* See 'Functions of Bounded Variation,' § 9, p. 63; 'Semi-integrals and Oscillating Successions of Functions,' § 2, p. 288.

† There is no difficulty in proving this theorem, which follows from § 14, Cor., p. 299, of "Semi-integrals."

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§ 8. We now have the following theorem :—

Theorem.—*If in the Fourier series of a function of bounded variation, and in its allied series, we substitute* $n^{-q}a_n$ *for* a_n, *and* $n^{-q}b_n$ *for* b_n, $(0 < q < 1)$, *each of the series so obtained is the Fourier series of an integral.*

This result is, in fact, an immediate consequence of the preceding corollary applied to the expressions of § 5.

§ 9. We must now obtain another result in parametric integration.

Theorem.—*If* $f(t)$ *is a function—of course continuous—satisfying the generalised Lipschitz condition that, for all values of* $\delta < d$, *where* d *is some fixed quantity in the completely open interval* (0, 1),

$$|f(t+h)+f(t)| < B|h|^{\delta},$$

B being a fixed quantity independent of t *or* h, *then*

$$\int_0^1 t^{q-1} f(x+t)\,dt \quad \text{and} \quad \int_0^1 t^{q-1} f(x-t)\,dt$$

are integrals, when regarded as functions of x, *provided only that* $q > 1-d$.

Select any quantity $q > 1-d$ and less than unity, then we can choose $\delta < d$, such that

$$(1-d) < 1-\delta < q.$$

Let us replace the inferior limit of integration by e, and integrate by parts. Then with the notation already adopted we have

$$\Big[\mathrm{F}(x+t)\,t^{q-1}\Big]_e^1 + (1-q)\int_e^1 \mathrm{F}(x+t)\,t^{q-2}dt.$$

Subtract $\mathrm{F}(x+1)-\mathrm{F}(x+e)$, and this expression plainly takes the form

$$(1-q)\int_e^1 t^{q-2}\{\mathrm{F}(x+t)-\mathrm{F}(x+e)\}\,dt,$$

of which the differential coefficient with respect to x is

$$(1-q)\int_e^1 t^{q-2}[f(x+t)-f(x+e)]\,dt,$$

since the integrand of this last integral is bounded, so that the preceding integral may be differentiated under the integral sign. Using our Lipschitz condition, we see that this differential coefficient is, numerically,

$$\begin{aligned}
&\leq (1-q)\int_e^1 t^{q-2}\mathrm{B}(t-e)^{\delta}\,dt,\\
&\leq \mathrm{B}(1-q)\int_e^1 (t^{\delta}+e^{\delta})\,t^{q-2}dt,\\
&\leq \mathrm{B}(1-q)(1-e^{\delta+q-1})/(\delta+q-1)+\mathrm{B}e^{\delta}(1-e^{q-1}),\\
&\leq \mathrm{B}\frac{1-q}{\delta+q-1}+\mathrm{B}e^{\delta},\\
&\leq \mathrm{B}\delta/(\delta+q-1),
\end{aligned}$$

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since $1-\delta < q$. Hence the differential coefficients with respect to x of

$$g_e(x) = \int_e^1 t^{q-1} f(x+t)\, dt - \mathrm{F}(x+1) + \mathrm{F}(x+e) \qquad (1)$$

form, as e diminishes, a succession which is bounded above and below. Hence,* if we integrate these differential coefficients between the limits 0 and x, the upper and lower limits of the integrals are integrals. But, since $\frac{d}{dx} g_e(x)$ is bounded, we know by Lebesgue's theorem that

$$\int_0^x \frac{d}{dx} g_e(x)\, dx = g_e(x) - g_e(0),$$

which converges to

$$\int_0^1 t^{q-1} f(x+t)\, dt - \mathrm{F}(x+1) + \mathrm{F}(x) - \int_0^1 t^{q-1} f(t)\, dt + \mathrm{F}(1) - \mathrm{F}(0),$$

when e approaches zero as limit. This last expression is therefore, when regarded as a function of x, an integral. Hence $\int_0^1 t^{q-1} f(x+t)\, dt$ is also an integral, and similarly $\int_0^1 t^{q-1} f(x-t)\, dt$ is an integral, when regarded as a function of x. Since q has been taken to be any quantity between $1-d$ and unity, this proves the theorem when $q < 1$. The same argument, with insignificant modifications, proves the theorem when $q > 1$.

Cor.—*Under the same circumstances, provided only in addition the integral of f oscillates finitely,*

$$\int_0^\infty t^{q-1} f(x+t)\, dt$$

is, when regarded as a function of x, an integral.

§ 10. The result of the preceding corollary gives us at once the following theorem :—

Theorem.—*If we substitute $n^{-q}a_n$ for a_n, and $n^{-q}b_n$ for b_n, in the Fourier series and allied series of a function satisfying the generalised Lipschitz condition that*

$$|f(t+h) - f(t)| < \mathrm{B}|h|^\delta,$$

for all values of δ less than d, where d is a fixed quantity in the completely open interval (0, 1), the series so obtained are the Fourier series of integrals, provided only that $1-d < q$.

This follows from the expressions, already used repeatedly, giving the Fourier functions of the new Fourier series, obtained by the process described.

* W. H. Young, "Semi-integrals and Oscillating Successions of Functions," 'Lond. Math. Soc. Proc.,' 1910, Series II, vol. 9, p. 301.

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§ 11. So far, in our process of generating Fourier series, we have always divided the coefficients a_n and b_n by positive powers of n. We have now to examine the effect in one or two classes of cases of the process of multiplying by such a factor.

Theorem.—*If we substitute $n^q a_n$ and $n^q b_n$ for a_n and b_n in the Fourier series of a function satisfying the generalised condition of Lipschitz, that for all positive values of δ less than a fixed quantity d less than unity,*

$$|f(t+h)-f(t)| < B|h|^\delta,$$

and, in the allied series, the series so obtained are both Fourier series, provided only q is less than d.

In fact, we may suppose the process performed in two stages. To prove that the process performed on the Fourier series leads to another Fourier series, we start with the allied series, and, choosing any value of $q < d$, divide a_n and b_n by n^{1-q}. We thus get, since $1-d < 1-q$, by § 10,

$$G(x) = \sum_{n=1}^{\infty} n^{-1+q} \{-a_n \sin nx + b_n \cos nx\},$$

where $G(x)$ is an integral. But this is the necessary and sufficient condition* that the series

$$-\sum_{n=1}^{\infty} n^q (a_n \cos nx + b_n \sin nx)$$

should be a Fourier series. This, therefore, proves the required result.

Similarly, starting with the Fourier series, we have

$$H(x) = \sum_{n=1}^{\infty} n^{-1+q} (a_n \cos nx + b_n \sin nx),$$

where $H(x)$ is an integral. But this is the necessary and sufficient condition that the series

$$\sum_{n=1}^{\infty} n^q (-a_n \sin nx + b_n \cos nx)$$

should be a Fourier series. This proves the statement as to the allied series.

Thus, both parts of the theorem are true.

§ 12. A precisely similar argument to that used in § 11 proves the corresponding result for the Fourier series of a function of bounded variation.

Theorem.—*If in the Fourier series of a function of bounded variation, and in its allied series, we substitute $n^q a_n$ for a_n, and $n^q b_n$ for b_n, where $0 < q < 1$, we shall always get series of Fourier.*

We use, in fact, the theorem of § 8 instead of that of § 10. The argument of § 11 is otherwise unaltered.

* *Loc. cit.*, "On the Condition that a Trigonometrical Series should have the Fourier Form," p. 423.

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§ 13. We have seen that, if f is a function satisfying a d-Lipschitz condition, then

$$\int_0^\infty t^{-q}[f(x+t)-f(x-t)]\,dt$$

$$= 2\sin\tfrac{1}{2}(1-q)\pi\,.\,\Gamma(1-q)\sum_{n=1}^{\infty} n^{-1+q}(-a_n\sin nx+b_n\cos nx),$$

provided $1-d<1-q<1$, that is, provided $0<q<d$.

We then have

$$C\frac{d}{dx}\int_0^\infty t^{-q}[f(x+t)-f(x-t)]\,dt \sim \sum_{n=1}^{\infty} n^q(a_n\cos nx+b_n\sin nx), \tag{1}$$

where

$$1/C = -2\cos\tfrac{1}{2}q\pi\,.\,\Gamma(1-q). \tag{2}$$

But $f(x)$ is a bounded and continuous function, and

$$f(x)\sim\sum_{n=1}^{\infty}(a_n\cos nx+b_n\sin nx).$$

Hence,* since $\Sigma n^q(a_n^2+b_n^2)$ cannot oscillate, it must converge, and its sum is given by

$$\sum_{n=1}^{\infty} n^q(a_n^2+b_n^2) = \frac{C}{2\pi}\int_{-\pi}^{\pi}dx\,.\,f(x)\frac{d}{dx}\int_0^\infty t^{-q}[f(x+t)-f(x-t)]\,dt, \tag{3}$$

provided only that $q<d$.

Hence also, if a_n', b_n' be the Fourier constants of another function f' satisfying a d'-Lipschitz condition, we can, if $2q<d+d'$, find q_1 and q_2, so that $2q<q_1+q_2<d+d'$, $q_1<d$, $q_2<d'$. We then have

$$n^q(a_na_n'+b_nb_n') \le n^{\frac{1}{2}(q_1+q_2)}(a_na_n'+b_nb_n') < n^{q_1}(a_n^2+b_n^2)+n^{q_2}(a_n'^2+b_n'^2),$$

so that the series of which the general term is

$$n^q(a_na_n'+b_nb_n')$$

is convergent.

Hence, by the same theorem as that used above,

$$\sum_{n=1}^{\infty} n^q(a_na_n'+b_nb_n') = \frac{C}{2\pi}\int_{-\pi}^{\pi}dx f'(x)\frac{d}{dx}\int_0^\infty t^{-q}[f(x+t)-f(x-t)]\,dt, \tag{4}$$

C being given by (2), and $2q$ being $<d+d'$.

Similarly,

$$\sum_{n=1}^{\infty} n^q(a_nb_n'-a_n'b_n) = \frac{K}{2\pi}\int_{-\pi}^{\pi}dx f'(x)\frac{d}{dx}\int_0^\infty t^{-q}[f(x+t)-f(x-t)], \tag{5}$$

where

$$1/K = 2\sin\tfrac{1}{2}q\pi\,.\,\Gamma(1-q) \tag{6}$$

and $2q<d+d'$.

* W. H. Young, "On the Integration of Fourier Series," 'Lond. Math. Soc. Proc.,' 1910, Series II, vol. 9, p. 456, § 7.

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Bearing in mind that* $n^q a_n^2$ and $n^q b_n^2$ are the Fourier constants of a continuous function, and that $n^q a_n$ and $n^q b_n$ are the Fourier constants of a function which is summable, we deduce the sums of the evidently convergent series

$$\Sigma\, n^{2q}\, a_n^3 \quad \text{and} \quad \Sigma\, n^{2q}\, bn^3.$$

Similarly, we can write down the sum of

$$\Sigma\, n^{3q}\,(a_n^4 + b_n^4)$$

and it is clear that this process can be repeated indefinitely, as well as varied in a variety of ways. We have only to make use of the theorems in the three papers cited.†

§ 14. It should be noted that our process will not change the Fourier series of a continuous function of the most general type into that of a function of bounded variation, still less into that of an integral. To see this, we have merely to consider the function of Weierstrass,‡ defined as the sum of the Fourier series

$$\sum_1^\infty a^n \cos b^n x,$$

where $a < 1$, b is an odd integer, and $ab > 1 + \frac{3}{2}\pi$. Evidently, if we write $(b^n)^{-q} a_n$ for a_n, the series takes the form

$$\sum_1^\infty (ab^{-q})^n \cos b^n x.$$

Now $(ab^{-q})\, b = ab^{1-q}$ is greater than $1 + \frac{3}{2}\pi$, however near unity q may be if b is chosen suitably. Thus the new series belongs to the same type as the Fourier series with which we started. It represents accordingly a function which is nowhere differentiable, and cannot therefore be a function of bounded variation.

In particular, then, we see that Weierstrass's function, though continuous, does not satisfy the generalised Lipschitz condition.

§ 15. We have seen in § 4 that if, for some positive quantity p, however small, $[f(t)]^{1+p}$ is summable, the process of dividing a_n and b_n by n^q, where $q > 1/(p+1)$ leads to the Fourier series of a continuous function. It at once follows that $\Sigma\, n^{-q}(a_n^2 + b_n^2)$, where $q > 1/(p+1)$, can at most only oscillate finitely, since the series converges when summed in the Cesaro

* W. H. Young, "On a Class of Parametric Integrals, etc.," §§ 6 and 12.

† The two just cited, and the paper on "Fourier Constants."

‡ K. Weierstrass, 'Abh. aus der Funktionenlehre,' 1886, p. 97, *seq.* See also Hobson's 'Theory of Functions of a Real Variable.'

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way. Hence, as each term is positive, so that the series cannot oscillate, it must converge. Moreover, we have

$$\sum_{n=1}^{\infty} n^{-q}(a_n^2+b_n^2) = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x)\,g(x)\,dx,$$

where, by § 4,

$$2\cos\tfrac{1}{2}q\pi\,.\,\Gamma(q)\,.\,g(x) = \int_0^{\infty}[f(x+t)+f(x-t)]\,t^{q-1}dt,$$

provided only $q > 1/(p+1)$.

It will be noticed that, for $p = 1$, this gives us information as regards the convergency of the series far inferior to that we already possess. We have, however, no reason to suppose that, if $p < 1$, any theorem as striking as that for $p = 1$ holds. In the case in which $p < 1$, the above result affords us in any case a material addition to our existing knowledge.

A Silica Standard of Length.

By G. W. C. Kaye, D.Sc., B.A.

(Communicated by R. T. Glazebrook, F.R.S. Received May 25,—Read June 29, 1911.)

(From the National Physical Laboratory.)

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1. *Materials for Standards of Length.*

The paramount qualities which must characterise a material suitable for a primary standard of length are constancy and durability. In addition to

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the absence of secular variation it should exhibit no linear thermal hysteresis, *i.e.* no lagging of length behind temperature. The ideal material would furthermore, from the operator's point of view, possess a zero coefficient of expansion—a convenience which, until recent years, has not been even approximately satisfied—should take a high polish, permit the ruling of suitable lines, and should answer all requirements as to hardness, elasticity, density, resistance to oxidation, etc.

These qualifications lead us to look for a pure substance—chemically simple—which will combine in itself as many as possible of the important essentials. In this connection it will be interesting to take notice of some of the materials which have been used at different times for primary line standards of length.

Material.	Density.	Coefficient of linear expansion.	Used for.
		Per degree C.	
Bronze (Baily's metal—32Cu, 5Sn, 2Zn)	8·7	$17·7 \times 10^{-6}$	British imperial standard yard.
Platinum	21·5	8·9	Mètre des archives.
Platinum-iridium (90Pt, 10Ir)	21·6	8·7	International prototype metre.
Nickel	8·9	12·8	
Steel	*c.* 7·8	*c.* 11	
Nickel-steel (43 per cent. Ni)	*c.* 8·2	8·0	Primary master standards of Japan and Russia.

The Imperial Standard Yard was made of *bronze* in 1843, and it has since been found by intercomparison with its official copies, also of bronze, that variations have arisen in the lengths of the different bars.* Copper alloys are now regarded as unsuitable for the purpose; they combine a large expansion coefficient with a secular length change, due to some molecular rearrangement, which is largely dependent on the temperature treatment. It was for this reason that a platinum-iridium copy of the yard was made in 1902.

The original metre—the Mètre des Archives—was constructed of *platinum* by Borda in 1795. Platinum enjoys the advantage of being but little affected by time or circumstance, but on the other hand it is expensive, soft, and inconveniently heavy.

When the International Prototype Metre was constructed in 1887, the difficulty as to the softness of platinum was met by alloying it with 10 per cent. of iridium, and the objection to the weight was overcome by

* In two cases the relative variation in 10 years was nearly 4 microns, *i.e.* about 4 parts in a million. See 'Memorandum on a New Copy of the Imperial Standard Yard,' H. J. Chaney, 1905, pt. 1, p. 30.

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substituting the "Tresca" or approximately X-shaped cross-section. Elaborate care was taken in refining and in artificially ageing the material, but one cannot refrain from feeling that it must, if only to a small extent, exhibit some of the defects of an alloy.

The platinum-iridium alloy admits of a high polish and permits the ruling of good lines. Its density is about two and a-half times, and its expansion coefficient about one-half, that of brass. Young's modulus is 2×10^{12} dynes/cm.^{2}, about the same as for mild steel.

Of all the pure metals, ordinarily available, and reasonably expensive, *nickel* is probably the most suitable for a standard of length. It is hard, does not tarnish, is about as elastic as steel, takes a high polish, and allows the ruling of excellent lines. A nickel standard of H section at the National Physical Laboratory has shown an increase in length in five years of only one part in 10 millions—a remarkably good stability. Nickel labours under the disadvantage at present that it is difficult to work. It is not easy to roll into tapes, and it is almost impossible to obtain a nickel line standard longer than 1 metre.

As to *steel*, whatever advantages it can offer, they are more than counterbalanced by its tendency to rust. Steel tapes have the great advantage of lying flat and straight, they will take a good graduation, and are not liable to kink under slight provocation. In field work, however, where accurate temperature measurements are practically impossible, the relatively high coefficient of expansion of steel puts tapes of this material out of court for the best work.

Invar.—The researches of M. Guillaume on the alloys of nickel and steel have, as is well known, culminated in invar, the 36 per cent. Ni alloy, which by reason of its low expansion coefficient at ordinary temperatures has received very extended application for many purposes. Invar enjoys further advantages—it does not readily rust and it will take a high polish—desiderata for line measures and tapes. On the other hand, it is not a permanent alloy, and it is impossible to ensure a specified coefficient of expansion, since a very slight variation in the composition is sufficient to produce considerable alteration in the expansibility. It is in consequence doubly important in the case of a long measure such as a tape, to look out for the effects of local heterogeneity, and it is more than usually dangerous to employ an expansion coefficient derived from a short sample of the material.

In practice, invar, procurable as such, is found to have a range of linear expansion coefficients of from about $-0{\cdot}3 \times 10^{-6}$ to $+2{\cdot}5 \times 10^{-6}$, the smallness of the coefficient being the criterion of the quality.

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Very occasionally a negative coefficient so large as -1×10^{-6} is found, and there is, of course, no difficulty in finding nickel steels approximating to invar with much larger positive coefficients than $+2{\cdot}5\times10^{-6}$.*

Invar is not very easy to work; it is somewhat soft and indifferently elastic. Young's modulus is about $1{\cdot}4\times10^{12}$ dynes/cm.^{2}, *i.e.* about two-thirds of that of steel. A deep scratch or a bad kink is usually followed by fracture.

Invar exhibits a considerable and gradual increase of length with time,† though much (but not all) of this may be eradicated by suitable annealing. This secular variation may be considerably accentuated by shocks.

The coefficient of expansion does not seem to vary appreciably with time, nor is it affected by shocks or artificial ageing. Bearing in mind the unstable character of invar, one would expect it to exhibit very appreciable thermal hysteresis, and, as Guillaume himself showed, this is the case.

Thermal hysteresis of length may be defined quantitatively as follows:— Let l be the length of a specimen which has been long maintained at 0°. It is subjected to a rise of temperature of $t°$, and is kept at that temperature long enough for equilibrium to be attained. If, when the temperature is lowered once more to 0°, the length after a short time is found to be $(l+\delta l)$, then $\frac{\delta l}{l}\cdot\frac{1}{t}$ is taken as the measure of the linear thermal hysteresis H. Thus H may be regarded as a residual variation of the expansion coefficient.

Guillaume represents his results on the hysteresis of invar by a parabolic curve connecting residual length variation with temperature

$$\delta l/l = -3{\cdot}25t^2\times10^{-9},$$

whence

$$\mathrm{H} = -3{\cdot}25t\times10^{-9}.$$

Thus if $t = 30°$, the final length of an invar metre after the cycle would be about 3 microns (3×10^{-6} metre) shorter than the initial length. But in

* The following linear expansion coefficients, determined at the National Physical Laboratory, may be of interest:—

Per cent. Ni.	Expansion coefficient.	Per cent. Ni.	Expansion coefficient.	Per cent. Ni.	Expansion coefficient.
0	*c.* $11{\cdot}0\times10^{-6}$	30	$12{\cdot}0\times10^{-6}$	50	$9{\cdot}7\times10^{-6}$
10	13·0	36 (invar)	0·9 (mean)	80	12·5
20	19·5	40	6·0	100	12·8

† An invar metre at the National Physical Laboratory, which has a mean coefficient of expansion of $1{\cdot}1\times10^{-6}$, has changed its length approximately according to the parabolic relation $\Delta l = \sqrt{32y} - 2{\cdot}1$, where Δl is the lengthening in microns (10^{-6} metre) over a period of y years reckoning from April, 1902, when it was annealed.

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this case, it must be remembered, sufficient time has to be allowed for equilibrium to be established at the higher temperature.

Now Guillaume has noticed that the higher the temperature the more rapidly does invar attain equilibrium. "Equilibrium is established seven times more rapidly for each 20° rise of temperature," and the case is one of a wide class of chemical reactions.* So that with a cycle of temperatures of moderate range and conducted in a reasonably short time the hysteresis of invar would not attain its full value, but only some exponential fraction of it.

It will be seen that while invar has brought with it many conveniences, we need for precision work a material free from its defects. The modern tendency in the case of nickel steels is to employ the 43 *per cent. Ni alloy*, which combines great stability with a moderate coefficient of expansion—about 8×10^{-6}, not unlike that of platinum. Both secular change and thermal hysteresis are extremely small. The 43 per cent. alloy rusts less readily than invar, and will take a high polish. It has a Young's modulus of about $1{\cdot}5 \times 10^{12}$ dynes/cm.^{2}. The temperature coefficient of electrical resistance is high, so that the temperature of a tape can easily be measured in this way.

Fused Silica.—The extremely small coefficient of expansion of fused silica would in itself commend it as a material for a standard of length. At ordinary temperatures the linear expansion coefficient is about $0{\cdot}4 \times 10^{-6}$, which with the exception of high quality invar is less than that of any other known substance.

The expansion curve of silica is shown in fig. 1,† and, as will be seen, is approximately straight from about 0° to 1000°. There is a length minimum at about −80° C., and a maximum (accompanied by a change point) at 1200° C. The coefficient of expansion rises to a slight maximum at about 500°.

The mean linear expansion coefficient between 0° and t° C. may be represented over the range 0° to 50° C. by

$$\alpha_t = (0{\cdot}39 + 0{\cdot}0012t)\,10^{-6};$$

for the range −50° to 0° C.

$$\alpha_t = (0{\cdot}39 + 0{\cdot}002t)\,10^{-6}.$$

* It is, for example, a matter of common observation in accurate mercury thermometry how the rate of establishment of equilibrium of a glass varies with the temperature. To secure, for instance, the full depression of the zero after 100° requires 20 minutes' heating at 100°. Most of the change is complete after one minute; but at, say, 10°, equilibrium is not attained until after several days. The result is that zero points taken immediately after 10°, 50°, 100°, ..., are all different, but, owing to the rapidity with which glass settles down at 100°, the 100° point remains perfectly fixed and unaffected by previous heat treatment. The changes are slower the more complex the glass.

† See Kaye, 'Phil. Mag.,' 1910, p. 718.

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Thus one of the qualifications of a material for a length standard—that of a small coefficient of expansion—is satisfied by fused silica. As regards thermal hysteresis one would, by analogy with glass (see footnote on p. 434), expect silica to be very good by reason of its chemically simple nature, and this view was borne out by experiments carried out by Mr. L. F. Richardson at the National Physical Laboratory.

Specimens of annealed fused silica, both clear and translucent, were

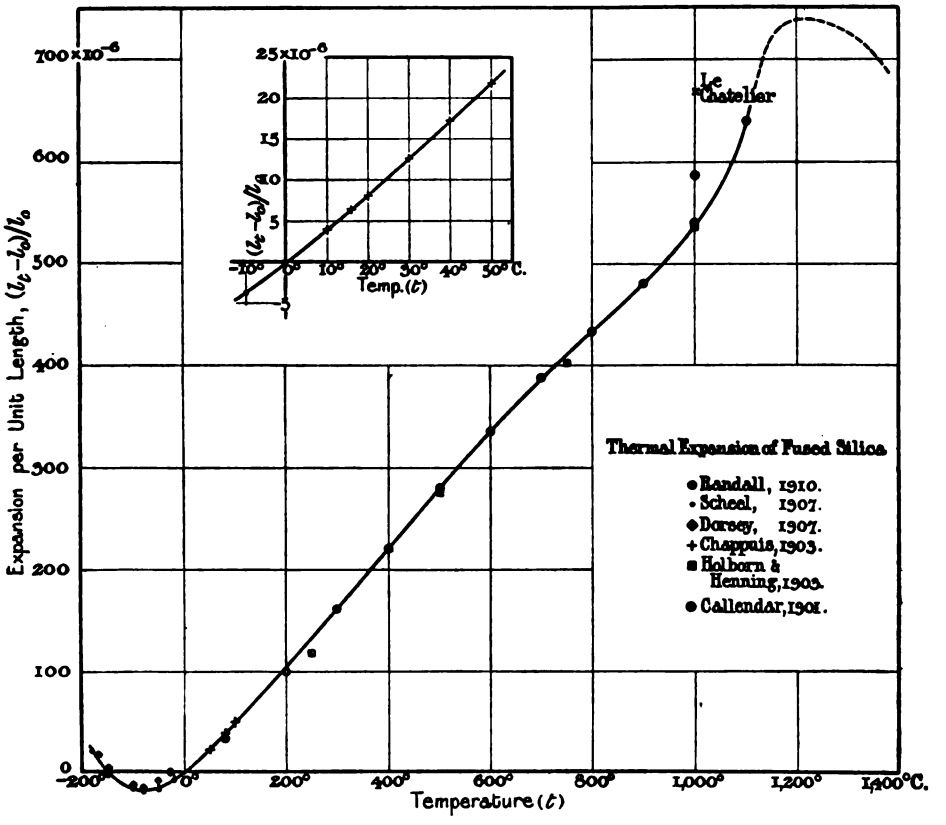

FIG. 1.

obtained in the form of end-measure rods about 45 cm. long. They were subjected for periods of from 1 to 90 hours to various temperatures over a range of from about −190° to 800° C. The values for the thermal hysteresis H (as defined above) are tabulated below. For the sake of comparison, the figures for invar and some common thermometry glasses (specially designed to show a small after-effect) are added. The glasses are in order of increasing complexity of composition.

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Substance.	Temperature range (t).	Hysteresis.	Authority.
	° C.		
Fused silica	0 to −190	0×10^{-9}	Nat. Phys. Lab.
,, ...	0 to 50	0	,, ,,
,, ...	0 to 400	0 to −5	,, ,,
,, ...	0 to 800	−17	,, ,,
Invar	0 to 50	−162 (1)	Guillaume.
Jena 59''' (5)	0 to 50	+23 (2)	Thiesen and Scheel.
Jena 16''' (5)	0 to 50	+42 (3)	,, ,,
Verre dur (5)	0 to 50	+56 (4)	,, ,,

(1) Derived from $H = -3{\cdot}25t \times 10^{-9}$.
(2) Derived from $H = (27-0{\cdot}08t)\,10^{-9}$.
(3) Derived from $H = (34+0{\cdot}16t)\,10^{-9}$.
(4) Derived from $H = (53+0{\cdot}05t)\,10^{-9}$.
(5) Jena 59''': 72 per cent. SiO_2, 11 per cent. Na_2O, 5 per cent. Al_2O_3, 12 per cent. B_2O_3.
Jena 16''': 67 per cent. SiO_2, 14 per cent. Na_2O, 7 per cent. CaO, 12 per cent. ZnO, Al_2O_3, and B_2O_3.
Verre dur: 71 per cent. SiO_2, 12 per cent Na_2O, 14 per cent. CaO, ½ per cent. K_2O, 2 per cent. Al_2O_3 and MgO.
It will be noticed that Jena 59''' has the simplest composition and the smallest value of H.

Thus the hysteresis exhibited by silica was small and negative after high temperatures, and was too small to be measured after moderate temperatures. In fact, for the ordinary temperature treatment to which a silica length standard is likely to be subjected, H may be regarded as negligible. It should be borne in mind that these results refer to annealed silica. Specimens subjected to a first heating frequently behave anomalously and show larger values of H, which, however, assumes a normal value for subsequent heatings. Thus annealing must form a part of the history of a silica length standard.

In respect of both expansibility and hysteresis there is practically nothing to choose between the different kinds of fused silica: the cheaper air-streaked satin-like variety is as good as the more expensive clear transparent kind. Neither kind can be regarded as costly.

Both varieties satisfy thus far the conditions we have enumerated as desirable in a material for a length standard. Young's modulus is about 5×10^{11} dynes/cm.^{2}, about half that of brass; but, on the other hand, the density of silica is low, about 2·2. The tensile strength appears to be of the order of 10^{10} dynes/cm.^{2}, which is a little less than half that of piano wire.

Silica is, of course, unaffected by oxidation; its durability is undoubted. It is a little harder than, and about as brittle as, glass, but the care which is naturally bestowed on a primary standard would act as a safeguard against the possibility of disaster arising from fracture.

The solubility in water appears to be of the order of 1 part in 100,000,

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which, though slight, suggests that the reference lines on a silica line standard should be protected, if it is to be used in water.

We come now to the ability of silica to take good reference lines. It can, of course, be ground and optically worked. With a suitable diamond there is no difficulty in ruling sharp-edged lines on silica which are sufficiently fine and definite for the purpose. The diamond requires to be very lightly loaded and the ruling should be done extremely slowly.

But two objections appear to the ruling of lines on the bare silica. One is the shelling or flaking of the edges of the lines which occurs within a day or two of their ruling, and effectually prevents their use for any kind of precision measurement. The other is the great difficulty of seeing the lines at all when the silica is immersed in water. The refractive indices of silica and water are not very different. The rapid deterioration of the rulings might conceivably be eradicated by immediate annealing or by the use of an exceptionally hard ruling diamond.

Various methods of illumination were tried to increase the visibility of the lines when immersed in water, and alternative suggestions, such as the insertion of invar plugs, were considered; but, finally, it was decided that the plan of coating the silica with a film of platinum and cutting the lines in the platinum offered the best prospects of success. Such a film could not affect the expansion of the silica.

The initial experiments were encouraging, and this last difficulty removed, the construction of a metre line-standard of fused silica was decided upon by the laboratory.

2. *Design of the Silica Metre.*

The final design for the silica standard took the form of a transparent silica tube a metre long, which merges at each end into a clear, transparent, horizontal slab of silica for taking the reference lines. As already mentioned, these lines are to be cut in a platinum film, and, although it is possible to get a very permanent and adherent film, it was decided for greater safety to protect the platinum by a cover-slip. If the reference lines are viewed through the cover-slip, the apparent length of the standard would be affected by any change with time of the tilt of the cover-slip. To avoid this, the plan was adopted of platinising the *under side* of the slab, cutting the graduation completely through the film, and viewing the line from above through the slab itself. In this way the light does not pass through the cover-slip, which is underneath the slab.

Considerations of stiffness and convenience suggested, for the body of the standard, tubing of about ¾ inch (18·7 mm.) external diameter and 1½ mm. thick. It was further decided, partly with the idea of preventing the tube

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rolling, to have silica supporting trunnions fused to the tube at one of the correct points of support, the other point to rest on a transverse roller in the usual way. Fig. 2 is an outline drawing (prepared from a photograph) of the bar with its trunnions and supports.

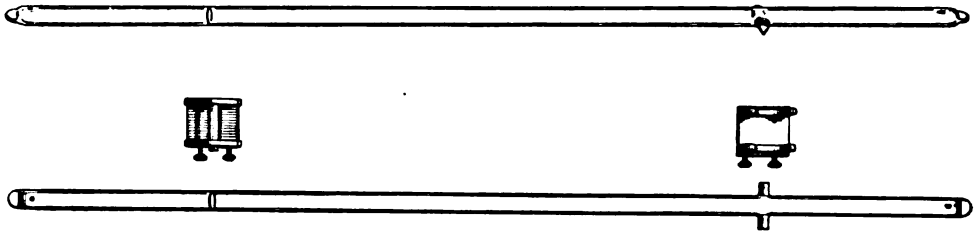

Fig. 2.

The under sides of the trunnions were ground to a blunt edge, the two portions of this edge being collinear to within 0·1 mm. The end slabs took the form of semicircular discs, which were made of specially clear silica, free from bubbles; both upper and lower surfaces were polished optically flat. The upper and lower surfaces of each end slab and the lower edge of the trunnion were constructed to be parallel to within 1 in 500 (*i.e.* to 7′) when the bar was properly supported.

Fig. 3 shows portions of the bar drawn to scale. The over-all length of the bar is 101·5 cm., and two holes, H (fig. 3), were provided to permit the submersion of the bar, which, without these, would have floated in water.

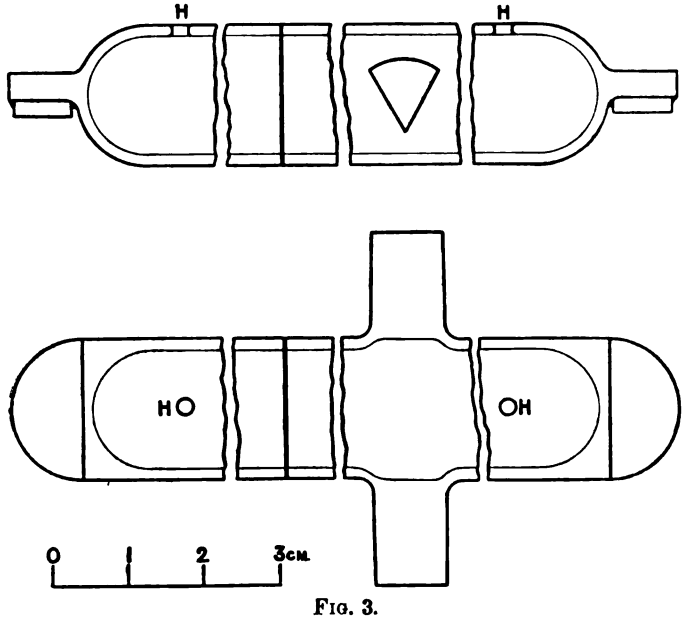

Fig. 3.

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It should be mentioned that the Silica Syndicate undertook the making of the standard, while Messrs. Hilger were responsible for the grinding and polishing of the trunnion and the end slabs.

3. *Positions of the Points of Support.*

If the length of a bar is always measured under the same conditions of use, then so long as these conditions can be exactly specified and reproduced we need not concern ourselves with the method of support and the effect of flexure on the length of the bar. However, a two-point support removes the uncertainty that exists as to pressure distribution when a bar not ideally straight rests on a surface not ideally flat; it has the further advantage with an immersed bar of assisting to promote uniformity of temperature. Now, as Airy* first recognised, it is desirable, from a practical standpoint, that the measured length should show a minimum susceptibility to accidental slight variations in the selected positions of the supports.

With this in mind, it follows, by the usual Bernoulli-Euler treatment, that for a long, uniform, homogeneous, isotropic bar on two symmetrically placed supports, the distance, a, between the supports should equal $l/\sqrt{3} = 0{\cdot}5773\,l$, where l is the length of the bar. This is, of course, a particular case of Airy's well-known formula $a = l/\sqrt{n^2-1}$, where n is the number of equidistant and symmetrically situated supports which divide the load equally.

Broch† has treated the question somewhat differently, and finds the most advantageous distance between the supports is given by $a = 0{\cdot}5594\,l$, which differs but little from the result by Airy's formula.

In the present case, since there are but two reference lines, which are situated, as near as may be, in the neutral plane of the bar, almost any convenient positions would serve for the two supports, provided these positions were adhered to. The constant difference between the actual length of the bar and its horizontal projection does not concern us. What we may most profitably seek is to minimise the effect on the constructed parallelism between the upper faces of the two end slabs, of any accidental inaccuracy in setting the moveable support. The Airy positions satisfy this condition provided the reference lines are not too far removed from the neutral plane. Our silica metre presents the case of a uniform bar with a trunnion at one point of support and an additional weight (that of the slab and its cover slip) at each end.

* Airy, 'Phil. Trans.,' 1857, p. 17.

† Broch, 'Trav. et Mém. du Bur. Intl.,' 1890, vol. 7, p. 362.

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If l is the length of half the bar,

a the distance of each support from the centre,

c the distance of the additional weight from the centre,

the slope of the bar at any point—distance x from the centre—which lies between the support and the end, is given by

$$\frac{1}{6EI}\left[w\{l(l^2-3a^2)-(l-x)^3\}+3W(c^2-a^2)\right],*$$

where E is Young's modulus,

I is the "area moment of inertia" of the cross-section about an axis through its C.G. and perpendicular to the plane of bending of the bar,

w is the weight of unit length of the bar,

W is the additional weight (*i.e.* the excess weight over the uniform value which obtains elsewhere).

In our case $x = l$, and $c = l$ (obviously the weight of the trunnion cuts out), and for the change of slope at the end of the bar to be nil

$$wl(l^2-3a^2)+3W(l^2-a^2) = 0,$$

whence

$$\left(\frac{a}{l}\right)^2 = \frac{3W+wl}{3(W+wl)}$$
$$= \tfrac{1}{3}\left(1+\frac{2W}{W+wl}\right).$$

In our case W is small compared with wl, so that

$$\frac{a}{l} = \frac{1}{\sqrt{3}}\left(1+\frac{W}{wl}\right).$$

From the dimensions of the standard, it was found that $W = \frac{1}{2}w$ is probably near the truth. Taking $l = 50$ cm., then

$$a = 28{\cdot}87\,(1+0{\cdot}01) = 29{\cdot}15 \text{ cm.},$$

so that the weight W introduces a 1 per cent. correction term into Airy's simple formula. Having regard to the unavoidable irregularity at the junction of each slab and the body of the tube, and the somewhat dubious assumption of perfect homogeneity, isotropy, and uniformity, we may take it that the round number 29 cm. is sufficiently accurate for the purpose.

At this point then, the trunnion was constructed, and 58 cm. from it a ring was etched round the tube as a permanent indication of the whereabouts of the other point of support. Silica is much less susceptible than glass to the action of hydrofluoric acid, and as the result of trials, about 3 hours' exposure to the strong acid (solution) was found to be suitable.

* See, for example, Chree, 'Phil. Mag.,' 1901, vol. 2, p. 598.

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4. *Position of the Plane of the Reference Lines.*

If P (fig. 4) is the reference line situated on the under side of the silica slab, then its apparent position is at I, where OIP is normal to the upper surface, and $OI = OP/\mu = \text{const}$, where μ is the refractive index.

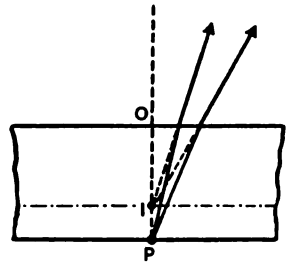

FIG. 4.

Since P is fixed relative to the silica, I also is a fixed point in the silica and is unaffected by the direction of viewing, provided it is approximately normal.

Now the Airy points of support are so arranged that the ends of the bar are horizontal, and therefore any small error in setting will produce only vertical movements of the points situated in the neutral plane at the ends of the bar. If therefore we arrange that I is in the neutral plane, small errors in setting, even though they change the tilt of the silica surface, do not cause any alteration in the distance II′ where I′ is the image of the reference line at the other end of the bar.

The idea was embodied in the design of the bar and thus the slabs are not symmetrical about the median horizontal plane of the metre, but are contrived so that when it is immersed in water the optical image of the reference lines shall lie in the neutral plane. The refractive index of silica relative to water is about 1·1, which means that with a slab 3·3 mm. thick, the image is lifted about 0·3 mm.

5. *Use of the Silica Standard in Air or Water.*

It would obviously be a convenience if the silica metre could be used indiscriminately in air or water, so that the one standardisation would suffice. But, for several reasons, the apparent length of the bar in air will be different from that in water unless the proper precautions are taken. This difference can arise from the following causes:—

(1) The different relative refractive index of the silica slab with reference to air and to water affects the position of the image of the reference line (see previous section), which cannot thus lie in the neutral plane of the bar in

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both cases. But as μ from silica to air is about 1·46, and μ from silica to water about 1·10, the displacement of the optical image in the slab (which is 3·3 mm. thick) will only amount to $\frac{3\cdot3}{1\cdot10}-\frac{3\cdot3}{1\cdot46}=0\cdot74$ mm.; so that any error which would be introduced on this score would be very small.

(2) A want of parallelism between the upper surfaces of the end slabs becomes important when the surrounding medium is changed. For, considering one slab, suppose the slope of the upper surface is ϕ, measured in a vertical plane containing the long axis of the bar. Then if the thickness of the slab is h, the reference line on the under side appears to be laterally displaced by an amount $h(\phi-\theta)$—see fig. 5—which may be written $h\phi(1-\mu^{-1})$,

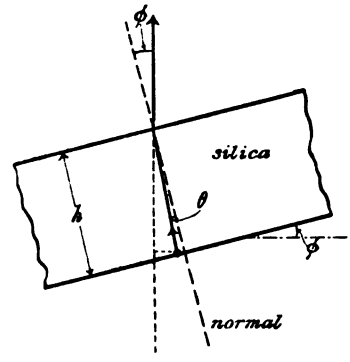

FIG. 5.

since θ and ϕ will always be small. The difference of the displacements in air and in water is

$$h\phi\,({}_w\mu_s^{-1}-{}_a\mu_s^{-1}),$$

where ${}_a\mu_s$ is the refractive index from air to silica,

${}_w\mu_s$ „ „ water „

Taking ${}_a\mu_s=1\cdot46$ and ${}_w\mu_s=1\cdot10$, then the difference of the displacements is $0\cdot225h\phi$. Thus, if h_1, ϕ_1, and h_2, ϕ_2, refer to the two end slabs, then the length of the bar in air differs from that in water by $0\cdot225\,(h_2\phi_2-h_1\phi_1)=\delta l$.

Writing $\phi_2-\phi_1=\delta\phi$,

$$\begin{aligned}\delta l &= 0\cdot225\,\{h_2(\phi_1+\delta\phi)-h_1\phi_1\}\\ &= 0\cdot225\,\{h_2\delta\phi+(h_2-h_1)\,\phi_1\}.\end{aligned}\qquad(A)$$

Now the standard of accuracy aimed at in this silica metre is 1 part in 10 millions, *i.e.* 1/10 micron. We require then that each of the two terms in the expression for δl shall be less than 1 in 20 millions; h is about 3·3 mm., so that, dealing only with the first term,

$$1000/(20\times10^6)=0\cdot225\times3\cdot3\times\delta\phi,$$

whence $\delta\phi$ must be less than 1 in 15,000.

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Messrs. Hilger were instructed to secure a parallelism of at least 8″ between the upper surfaces, *i.e.* 1 part in 25,000, the bar being properly supported.

(3) The method of setting up a bar for observation in a comparator ensures that the plane which contains both reference lines shall be horizontal; but, unless the surfaces of the two end slabs are coplanar, we shall have a state of things shown in fig. 6, in which both surfaces, although parallel, have to be tilted to secure the horizontality of the plane containing the reference lines P, P′.

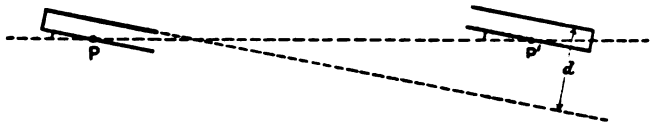

FIG. 6.

Thus, although $\delta\phi$ vanishes, ϕ may be appreciable, so that in the expression (A) above for δl, the term $(h_2-h_1)\,\phi_1$ may (if $h_1 \neq h_2$) become of importance, and should be provided for in the specification.

Consider, as an extreme case, when d (in fig. 6) = 1 mm., then $\phi_1 = 1/1000$.

Now the order of the first term $h_2\,\delta\phi$ in expression (A) is 3·3/25000 mm.; the order of the second term $(h_2-h_1)\,\phi_1$ should be no more than this.

Thus $$h_2-h_1 \not> \frac{3{\cdot}3}{25000} \times 1000, \quad i.e. \quad h_2-h_1 \not> 0{\cdot}13 \text{ mm.}$$

When the present bar was ordered, the importance of this condition had not been realised, and the length of the standard in water was subsequently found to exceed the length in air by 0·5 micron. In a later specification the following stipulations have been incorporated:—

(*a*) The upper surfaces of the two end slabs shall be coplanar to less than a millimetre over the length of the bar, *i.e.* d shall be less than 1 mm.

(*b*) The two end slabs shall have the same thickness to within 0·02 mm.

Obviously, this clause also provides for the unlikely case of the bar, as a whole, being used with an appreciable inclination to the horizontal.

Apart, however, from the convenience of being able to use the bar indiscriminately in air or water, there is little to urge in favour of the above somewhat stringent restrictions as regards the parallelism, thickness, etc., of the end slabs. At the National Physical Laboratory it is probable that the bar will almost always be used in water. We have, moreover, to remember that the annealing of the bar may have some slight effect on, at any rate, the parallelism of the slabs.

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6. *Platinising the End Slabs.*

As mentioned above, the under side of each slab is to be platinised, and accordingly a method of platinising was sought, which would give a bright surface on the side next to the silica, so that the lines, when viewed by reflected light in the usual way, would appear dark on a bright ground.

The method of cathodic sputtering in a vacuum tube can be used for producing metallic films of extreme thinness. Thick films are apt to peel unless very slowly deposited. The chief conditions for success are: (1) a pressure maintained low enough to yield a cathode dark space of, say, about 2 inches, just within which the body to be coated should be placed, and (2) a not too powerful discharge.

A disc cathode of platinum is convenient, and it is beneficial to put the body (previously cleansed) in metallic contact with the anode. A hydrogen atmosphere is advantageous, though usually enough hydrogen is expelled from the cathode during the discharge. The method has the advantage that it can be used at ordinary temperatures, but the films deposited in this way, though bright, are not strongly adhering, and will not withstand any sort of abrasion.*

Recourse was had therefore to the "liquid platinum" of Messrs. Johnson, Matthey & Co. This is a slightly gummy solution of a platinum salt, which, on ignition, is capable of yielding excellent deposits of platinum. These are ordinarily brightest on the side remote from the silica, but as the result of many trials it was found that, with the following precautions, a suitably bright, closely adhering film of platinum could be obtained with certainty.

The silica slab is cleaned to free it from grease, etc., and the solution is generously applied with a small camel-hair brush to the surface, which is then put on the slant and allowed to drain, the accumulated excess being removed after a few minutes. A clear transparent film of the "liquid platinum" is thus deposited evenly over the surface, and is allowed to dry slowly at room temperature for a day or so. It is finally dried off on an air or water bath. The silica slab is then inserted in a muffle furnace at a dull red heat (600° C.) and allowed to remain there for a few minutes. On withdrawal it will be found to be coated with a film of platinum which is almost equally brilliant on the two sides, but is, however, soft and readily detachable. The furnace temperature is raised to about 900° (bright cherry red), and the end of the bar re-inserted for two or three minutes; a longer time is apt to spoil the lustre. This treatment renders the platinum film hard and strongly adhering; it would, if necessary, stand burnishing with some soft

* Sir David Gill informs me that sputtered iridium films can be got hard and adherent.

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metal. The films thus prepared are semi-transparent, and should, when held up to the light, present a homogeneous and fine-grained structure.

If desired, a second film can in like manner be superimposed on the first. The method is unobjectionable on the score of the safety of the silica, which can be subjected to the sudden changes of temperature with impunity.

The necessity for employing such a high temperature in platinising made it desirable to carry out the annealing of the bar at a stage subsequent to the platinising, and this procedure was adopted.

7. *Ruling the Reference Lines.*

It was decided to rule the reference lines before annealing, in order to ascertain any effect that the annealing might produce on the length of the bar.

The lines were ruled by the laboratory dividing engine. Apart from the choice of a suitable diamond, the conditions for success are a light load and slow ruling. The comparatively soft platinum deposit, backed up by the harder silica, permits the ruling of very beautiful clean-edged lines. Almost any degree of fineness can be obtained by varying the load on the diamond, the fineness depending, of course, on the extent to which the diamond removes the platinum film. The method of observing the lines through the silica has the great advantage that the narrowest part of the furrow cut by the diamond is the only part that can be viewed by the microscope (fig. 7).

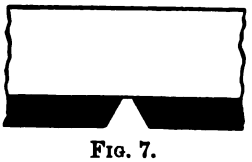

Fig. 7.

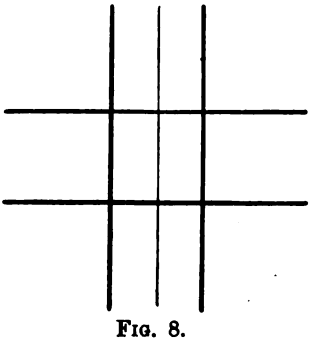

Fig. 8.

The lines lend themselves to work of the highest precision, and constitute a valuable addition to the advantages which the silica metre possesses. Comparison with the lines on the nickel and invar standards of the laboratory gives results entirely in favour of the lines on the silica standard.

For loads less than about 5 grm., the lines were inconveniently fine for use in comparator microscopes of 20 or 50 diameters magnification : a load of 7 grm. was finally adopted.

A couple of transverse "finder" lines, each 100 microns from the central

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transverse reference line, were inserted on each end slab. They were crossed at right angles by a pair of longitudinal lines about 200 microns apart. The part of the central transverse line which is contained within the two longitudinal lines is that which is used in measurement (fig. 8).

The silica metre was then compared with an invar metre, and its length was found to be $1{\cdot}000068_6$ metre at 18° C.

8. *Annealing the Silica Metre.*

A reference to the expansion curve of fused silica on p. 435 will show that at about 500° a not very pronounced maximum value of the coefficient of expansion is indicated. Quartz crystal at about the same temperature exhibits abnormally high expansion, and perhaps it would be right to infer that the maximum at 500° in the case of fused silica is a residual effect due to traces of unconverted quartz. However, the point, such as it is, is useful in setting a limit to the temperature that should be employed in annealing the silica metre. Moreover, the table on p. 436 shows that the thermal hysteresis exhibited by silica is much less for temperatures below about 500° than for higher temperatures. In the absence of any guiding information, it was decided to go no higher than about 450° in the annealing. Experience and future observation of the standard may indicate whether or not a lower temperature would be more advantageous.

For the purposes of the annealing, an electric furnace consisting of a Morgan fireclay tube wound with Eureka wire was constructed. The length of the tube was about 6 feet, its external diameter about $3\frac{1}{2}$ inches. The lagging was of magnesia brick and very ample. An exploring Pt-Ir thermocouple was used to calibrate the furnace, and showed that the temperature was approximately uniform throughout the central region employed.

A special fireclay carriage with silica contacts for the correct supports of the metre was built, and the metre was inserted into the furnace at room temperature. By suitable external resistance control, the temperature was raised in two days to about 450° C. This temperature was maintained for some eight days, after which about a fortnight was taken for the furnace to cool down slowly to room temperature.

The length of the metre after annealing was found to be $1{\cdot}000067_9$ metre at 18° C., which points to a shrinkage of a little over half a micron due to the annealing. This is extremely small after such severe temperature treatment, and gives support to the view that the future secular variation of the silica standard will be very slight. With this point in view, it is intended to keep the silica metre under close observation during the next few years.

Semicircular silica cover-slips were affixed under the end slabs by means of

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a cold cement kindly supplied by Mr. Chas. Baker. The joints were afterwards made water-tight at the edges by a mixture of red lead and linseed oil.

9. *Summary.*

The general properties of fused silica, and in particular its remarkably low coefficient of expansion, render this substance specially suitable for the construction of permanent length-standards of the highest class.

The coefficient of expansion of platinum-iridium, which has hitherto been the material almost exclusively employed in the best work, is about 9×10^{-6} per degree C., while that of silica over the ordinary range is about $0{\cdot}4 \times 10^{-6}$, *i.e.*, 1/20 of this amount. It is true that the best qualities of invar, M. Guillaume's nickel-steel containing 36 per cent. Ni, have expansion coefficients comparable with that of silica, but experience has shown that while invar is eminently useful for working standards, it is quite unsuitable for primary standards, owing to its large thermal hysteresis. Fused silica, on the contrary, has now been found to be practically entirely free from this defect; it enjoys, in the matter of cost, an enormous advantage over platinum-iridium; furthermore, in view of the fact that primary standards are always handled by trained and skilled observers, its comparative fragility is of small consequence.

Modern methods of manufacturing and working silica have rendered it possible to construct a silica line-standard metre. The present model, the first of its kind, consists of a silica tube into which are fused at its ends optically-worked plane parallel slabs of silica. These carry the graduations, and their undersides are platinised. The graduations defining the metre length are made by cutting through the platinum film with a ruling diamond. The platinum deposit permits the ruling of very beautiful clean-edged lines.

The bar is supported at the Airy points and so that the slabs are horizontal. The lines are viewed through the slabs from above, and are thus seen to advantage.

The apparent length of the standard is independent of any change of tilt of the cover-slips which are used to protect the platinum films. The thickness and position of the end slabs are so arranged that the image of each reference line lies in the "neutral plane" when the bar is immersed in water.

The writer wishes gratefully to acknowledge the continual kindly interest of Dr. R. T. Glazebrook, Director of the National Physical Laboratory. He would further record his thanks to Mr. J. E. Sears for very valuable criticism and advice at many stages in the work.

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The Distribution of Slide in a Right Six-face subject to Pure Shear.

By E. N. DA C. ANDRADE, B.Sc., Jessel Scholar of the University of London.

(Communicated by Prof. Karl Pearson, F.R.S. Received October 14, 1910; revised May 28, 1911,—Read June 29, 1911.)

Introductory.

The question of the exact distribution of slide in the cross-section of a body subjected to transverse force has recently attracted considerable attention in connection with the much-discussed problem of the stability of dams.* The experiments to be described were undertaken with a view to ascertaining this distribution in the simple case of a right six-face, one face of which is everywhere fastened to a fixed rigid plane, while the opposite face, also fastened to a rigid plane, is slid parallel to itself, all the other faces being free. The slide was measured over a free face parallel to the direction of traction by an optical method described in the experimental section. Engineering practice assumes the distribution to be parabolic, but this is generally discredited. The experimental work of Pearson and Pollard† indicated that when the shear was due to water pressure only, the distribution over a horizontal section had two maxima, and a minimum rather than a maximum at the centre. The experiments of Wilson and Gore‡ indicated a double maximum with certain forced distribution of shear over the base, but not with others. Hence it appeared desirable to test the matter *de novo* with a simpler load than occurs in a model dam, and a simpler contour; the rectangular contour was adopted as being of considerable theoretical interest, and possibly amenable to detailed mathematical treatment.

The result has been to obtain experimentally curves which leave no doubt as to the real existence of a double maximum distribution of slide; the double maximum is very marked over the central section, but, as would be expected, less strongly marked over the sections nearer to the faces constrained to remain plane. The curves resemble somewhat those obtained theoretically by Filon§ for a different system of loading, viz., a bar of rectangular cross-

* See, *e.g.*, Atcherly and Pearson, "On Some Disregarded Points in the Stability of Masonry Dams"; and Pearson and Pollard, "An Experimental Study of the Stresses in Masonry Dams," 'Drapers' Company Research Memoirs,' Technical Series, II and V.

† *Loc. cit.* See particularly dotted curves on Plate 8.

‡ Wilson and Gore, 'Institution of Civil Engineers,' vol. 172.

§ L. N. G. Filon, 'Phil. Trans.,' 1903, A 334. See p. 126.

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section, pressed on two parallel sides by two knife-edges not opposite to one another, and equilibrated by two shears over the free ends, which are at distances such that the principle of equipollent loading applies.

An attempt was made to see whether the solution of an analogous analytical problem could be approximately represented by using functions such as those indicated by Filon* and Dougall,† depending on roots of the transcendental equation $\sinh z = z$. A number of such solutions were taken, and the constants so chosen that the shift conditions were satisfied at a number of isolated points. The results are shown in fig. 5, and give variations of slide of the same general nature as those found experimentally, but the lack of closer agreement indicates that such solutions are probably inadequate to the complete solution of the problem. A discussion of the difficulties connected with this mode of representation will be found in the analytical section of the paper.

Experimental Method.

To measure the slide, the optical method described in the memoir on the stresses in masonry dams by Karl Pearson and A. F. C. Pollard, already quoted, was employed. The right six-face, whose approximate dimensions were 16 in. × 4 in. × 4 in., was cast out of the gelatine-glycerine jelly of which the model dams were made, and two of the larger parallel faces fixed to boards by means of fine copper gauze nailed to the wood and heated before the application of the jelly. Into one of the large free faces, fine needles were then inserted in rows 1 cm. apart, the needles in each row being 1 cm. apart; this was effected by laying a sheet of squared paper on the jelly, through which the needles were pushed, after which the paper was removed. The lower half of the face was thus prepared with five rows of needles, enabling measurements to be made along four lines. The microgoniometer employed was the one fully described in the above memoir, used in conjunction with a transparent vertical scale, a straight portion of the filament of an ordinary incandescent electric lamp being used as the source. One of the boards was firmly fixed to the table, while a horizontal pull could be applied to the upper one by a cord running over a pulley. So that the six-face might be subjected to pure shear, without bending moment, it was arranged that a vertical pull could be applied to one end of the upper horizontal face by a weight attached to a cord passing over a pulley; this,

* L. N. G. Filon, "On the Expansion of Polynomials in Series of Functions," 'Lond. Math. Soc. Proc.,' 1906, Ser. 2, vol. 4, Parts 5 and 6.

† J. Dougall, "An Analytical Theory of the Equilibrium of an Isotropic Elastic Plate," 'Trans. Roy. Soc. Edin.,' 1904, vol. 41, Part 1, No. 8.

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together with an equal weight placed resting on the other end of the face, gave a couple adjusted to be equal in magnitude to the shearing couple, and opposite in sign, so that there was no bending.

Preliminary experiments were made on the time-yield and recovery of the jelly under different loads, with the object of discovering the greatest load with which complete recovery could be obtained in a reasonable time. The goniometer was placed in position near the middle of the side and the block strained for some minutes and then unloaded, the scale readings being taken during straining and recovery. With loads of 8 lbs. and 6 lbs. there was a permanent set; with 4 lbs. load complete recovery could be obtained, and the increase of slide during the second minute after loading was only about 0·015 of the total slide. The shift of the upper face due to this load was about 0·33 mm., as measured directly with a micrometer.

The load adopted was therefore 4 lbs., with a corresponding couple to avoid bending. The microgoniometer being placed on three needles at a given place, this load was applied for a minute, readings being taken at 15, 30, and 45 seconds after loading, and at intervals of a minute for 5 minutes after the removal of the load. Complete recovery was seldom attained at the first series of readings on any particular set of needles, but generally with a second set of readings, the microgoniometer not being touched in between, recovery was obtained within the five minutes. For a given position the displacements of the first loading were probably necessary to make the microgoniometer settle down to a perfectly stable position on the needles; at any rate, two series of readings were taken at each place, the second being in general reliable. Occasionally a third set had to be taken; the criterion of reliability adopted was complete recovery within the five minutes.

The microgoniometer was placed successively on the different needles of the same horizontal row, and readings corresponding to both mirrors of the instrument taken in the manner described, one of the mirrors, of course, being very little deflected compared with the other. There were 36 and 37 needles respectively in alternate rows, and as preliminary experiments had shown that the readings varied from day to day at a given place (probably mainly owing to temperature, though hygrometric conditions may have something to do with it) it was judged desirable to do a complete row in one day, when, as a rule, readings taken for the same place at different hours agreed.

To give the angle of slide, these readings had to be corrected for the obliquity of the "horizontal" mirror ray by means of the formula given on p. 27 of the Pearson and Pollard memoir. When this had been done, the

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slide for the four different sections considered experimentally was plotted against the corresponding distance along the x-axis.

Experimental Results.

Within the limit of experimental error the curves were found to be symmetrical about a vertical through the mid-point of the side, as might be expected; only half of each curve is therefore shown. It is seen at once that the general result has been to demonstrate clearly that the shear curves have a double maximum, with a minimum at the centre, as the work of Pearson and Pollard seemed to indicate. The area of the curve, which gives a measure of the load, is not quite the same at all sections, as the elastic constants must vary with the temperature, and the different curves were obtained on different days. The greatest deflection was under 1 cm. on the scale, so, since the fractions of a millimetre were estimated by eye, an experimental error of at least 2 per cent. is probable. Small local variations may also be caused by the inevitable slight irregularities where the jelly was fastened to the boards, though it was trimmed as well as possible before experiments were made.

The thickness of the block was about 9 cm. vertically. The experimental measurements give roughly the mean slide over a strip of the face 1 cm. thick, and we take this as being the slide corresponding to the middle line of the strip. Then fig. 1 gives the distribution of slide along a line distant 4·5 cm. from the lower fixed face, and figs. 2, 3, and 4 the slide along lines distant 3·5, 2·5, and 1·5 cm. respectively. It will be observed that the central minimum is most marked over the mid-line, and that as we approach the rigidly fixed face we get, as we should expect, an approach to a uniform slide across the greater portion of the section. An important point is that secondary maxima are indicated, notably in figs. 1 and 3.

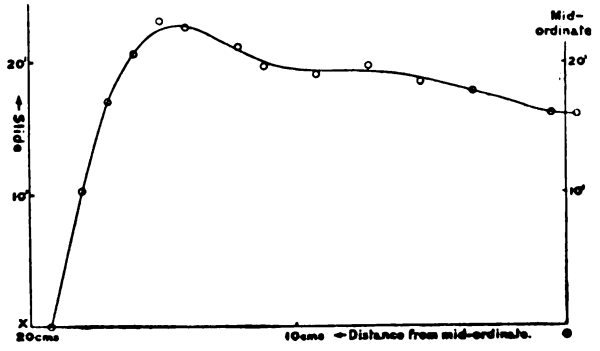

FIG. 1.

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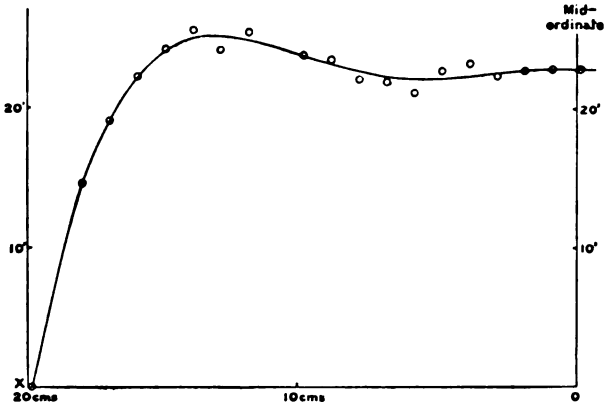

FIG. 2.

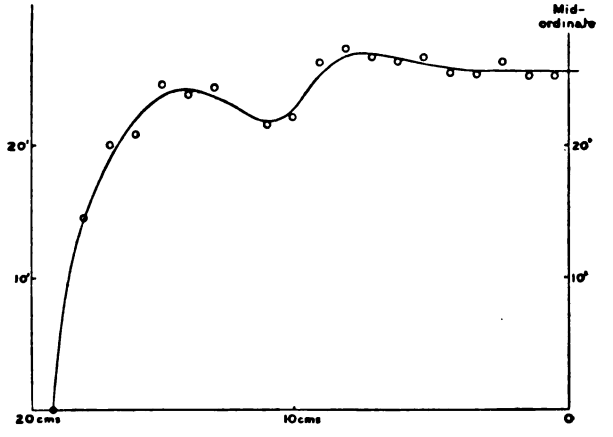

FIG. 3.

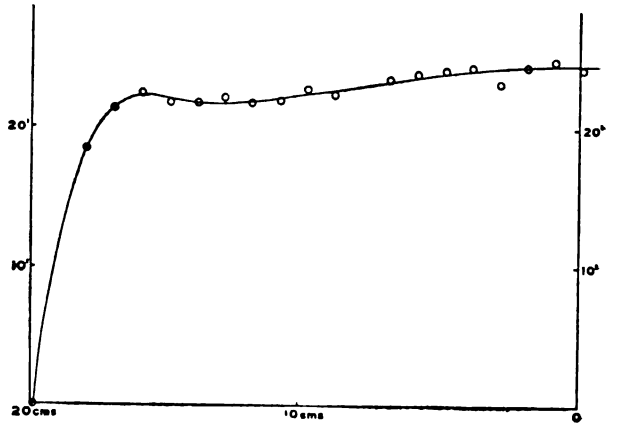

FIG. 4.

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Angle of Shear for the Four Sections.

Position.*	I.	II.	III.	IV.
1	10·4′	14·8′	14·7′	18·7′
2	17·2′	19·3′	20·8′	21·6′
3	20·9′	22·5′	21·1′	22·7′
4	23·4′	24·5′	24·9′	22·0′
5	22·9′	25·9′	24·1′	22·0′
6		24·4′	24·7′	22·4′
7	21·4′	25·7′		22·0′
8	19·9′		21·8′	22·2′
9		24·0′	22·4′	23·0′
10	19·3′	23·7′	26·6′	22·6′
11		22·3′	27·7′	
12	20·0′	22·1′	27·0′	23·7′
13		21·3′	26·7′	24·1′
14	18·8′	22·9′	27·0′	24·4′
15		23·4′	25·8′	24·6′
16	18·1′	22·5′	25·7′	23·4′
17		22·9′	26·7′	24·7′
18		23·0′	25·6′	25·1′
19	16·4′	23·0′	25·6′	24·5′
20	16·3′			

* The positions are read from the end of the row of needles: 1 corresponds to a distance of about 1·5 and 2 cm. from the free edge respectively for alternate rows.

Analytical Treatment of an Analogous Problem.

The following analytical attempt is concerned with the problem of an elastic right six-face, two parallel faces of which are given uniform shifts in their own planes in opposite directions, the remaining faces being free. For simplicity it has been necessary to take for the displacements and shifts their average values throughout the finite thickness of the block, in which case it is known* that the problem reduces to that of uniplanar stress, *i.e.* the problem of an indefinitely thin plate.

The notation used is that of Pearson and Todhunter's 'History of Elasticity.' Let the block be of length $2a$, depth $2b$, with axes taken through the mid-point. We then have

when $y = \pm b$, $\quad v = 0$;

when $y = \pm b$, $\quad u = \pm e$, say;

when $x = \pm a$, $\quad \widehat{xx} = \widehat{xy} = 0$.

In Love's 'Treatise on Elasticity' it is shown† that for generalised plane stress the stress can be expressed in terms of a stress-function χ, the formulæ for the stresses being

$$\widehat{xx} = \frac{\partial^2\chi}{\partial y^2}, \quad \widehat{yy} = \frac{\partial^2\chi}{\partial x^2}, \quad \widehat{xy} = -\frac{\partial^2\chi}{\partial x\,.\,dy},$$

* L. N. G. Filon, 'Phil. Trans.,' *loc. cit.* Also Love's 'Treatise,' Chap. IX.

† Love's 'Treatise,' Chap. IX.

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and for the displacements

$$2\mu u = -\frac{\partial \chi}{\partial x} + \xi, \qquad 2\mu v = -\frac{\partial \chi}{\partial y} + \eta,$$

where $$\frac{\partial \xi}{\partial x} = \frac{\partial \eta}{\partial y} = \frac{2(\lambda+\mu)}{3\lambda+2\mu}\nabla^2\chi \quad \text{and} \quad \frac{\partial \xi}{\partial y} = -\frac{\partial \eta}{\partial x}.$$

∇^2 denotes $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$, and with this notation χ must satisfy the equation

$$\nabla^4\chi = 0. \tag{1}$$

The conditions of the problem make u an even function of x and an uneven function of y; we assume, therefore, taking the sine in y,

$$\chi = (\mathrm{B}x \cosh nx + \mathrm{C} \sinh nx) \sin ny,$$

which is a known solution of (1).

This gives $\nabla^2\chi = 2n\mathrm{B} \sinh nx \sin ny$, whence we find

$$\xi = \frac{2(\lambda+\mu)}{3\lambda+2\mu} 2\mathrm{B} \cosh nx \sin ny$$
$$= \frac{2\mathrm{B}}{1+\sigma} \cosh nx \sin ny,$$
$$\eta = -\frac{2\mathrm{B}}{1+\sigma} \sinh nx \cos ny,$$

where $\sigma = \dfrac{\lambda}{2(\lambda+\mu)}$ = Poisson's ratio.

$$\widehat{xx} = \frac{\partial^2\chi}{\partial y^2} = -n^2(\mathrm{B}x \cosh nx + \mathrm{C} \sinh nx) \sin ny, \tag{2}$$

$$\widehat{yx} = -\frac{\partial^2\chi}{\partial x . \partial y} = -n\{\mathrm{B}(\cosh nx + nx \sinh nx) + \mathrm{C}n \cosh nx\} \cos ny. \tag{3}$$

For these stresses to vanish at $x = \pm a$, we have from (2)

$$\mathrm{C} = -\mathrm{B}a \coth na,$$

and, substituting in (3),

$$na = \sinh na \cosh na \quad \text{or} \quad 2na = \sinh 2na. \tag{4}$$

This is the transcendental equation for n given by Filon.*

$$2\mu u = -\frac{\partial \chi}{\partial x} + \xi$$
$$= -\mathrm{B}n\left(x \sinh nx - a\frac{\cosh^2 na + (1-\sigma)/(1+\sigma)}{\frac{1}{2}\sinh 2na} \cosh nx\right) \sin ny,$$

or if $-\dfrac{\mathrm{B}n}{2\mu} = \mathrm{A}$,

$$u = \mathrm{A}\left(x \sinh nx - a\frac{\cosh^2 na + (1-\sigma)/(1+\sigma)}{\frac{1}{2}\sinh 2na} \cosh nx\right) \sin ny, \tag{5}$$

* L. N. G. Filon, 'Lond. Math. Soc. Proc.,' *loc. cit.*

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$$v = A\left(-\frac{a\cosh^2 na - 2/(1+\sigma)}{\frac{1}{2}\sinh 2na} + x\cosh nx\right)\cos ny, \tag{6}$$

$$\frac{\widehat{xy}}{\mu} = A\sinh 2na\left(\frac{x}{a}\sinh nx - \tanh na\cosh nx\right)\cos ny. \tag{7}$$

Since n, determined from (4), is complex, we must rationalise these values of u, v, and $\widehat{xy}$ for numerical interpretation.

Let $\qquad 2na = \alpha + i\beta, \quad$ and take $\quad \sigma = 0{\cdot}25,$

(5), (6), and (7) finally give, as rationalised values for u, v, and $\widehat{xy}$,

$$\begin{aligned} u = \Sigma\Big[& L_1 \sin\frac{\alpha_1 y}{2a}\cosh\frac{\beta_1 y}{2a}\left\{x\sinh\frac{\alpha_1 x}{2a}\cos\frac{\beta_1 x}{2a}\right. \\ & -a\,\frac{\frac{1}{2}\sinh 2\alpha_1 + 2.2\alpha_1}{\cosh^2\alpha_1 - \cos^2\beta_1}\cosh\frac{\alpha_1 x}{2a}\cos\frac{\beta_1 x}{2a} \\ & \left.-a\,\frac{\frac{1}{2}\sin 2\beta_1 + 2.2\beta_1}{\cosh^2\alpha_1 - \cos^2\beta_1}\sinh\frac{\alpha_1 x}{2a}\sin\frac{\beta_1 x}{2a}\right\} \\ & -L_1\cos\frac{\alpha_1 y}{2a}\sinh\frac{\beta_1 y}{2a}\left\{x\cosh\frac{\alpha_1 x}{2a}\sin\frac{\beta_1 x}{2a}\right. \\ & -a\,\frac{\frac{1}{2}\sinh 2\alpha_1 + 2.2\alpha_1}{\cosh^2\alpha_1 - \cos^2\beta_1}\sinh\frac{\alpha_1 x}{2a}\sin\frac{\beta_1 x}{2a} \\ & \left.+a\,\frac{\frac{1}{2}\sin 2\beta_1 + 2.2\beta_1}{\cosh^2\alpha_1 - \cos^2\beta_1}\cosh\frac{\alpha_1 x}{2a}\cos\frac{\beta_1 x}{2a}\right\} \\ & +M_1\cos\frac{\alpha_1 y}{2a}\sinh\frac{\beta_1 y}{2a}\Phi_1(x) + M_1\sin\frac{\alpha_1 y}{2a}\cosh\frac{\beta_1 y}{2a}\Psi_1(x)\Big], \end{aligned} \tag{8}$$

where $\qquad \Phi(x) =$ first expression in brackets $\{\ \}$,

$\qquad\qquad \Psi(x) =$ second expression in brackets $\{\ \}$,

the suffix 1 indicates that the values are those for the first root of the equation $\qquad \sinh 2na = 2na,$

and the summation is to be taken for all roots of this equation.

$$\begin{aligned} v = \Sigma\Big[& L_1\cos\frac{\alpha_1 y}{2a}\cosh\frac{\beta_1 y}{2a}\left\{x\cosh\frac{\alpha_1 x}{2a}\cos\frac{\beta_1 x}{2a}\right. \\ & -a\,\frac{\frac{1}{2}\sinh 2\alpha_1 - 2.2\alpha_1}{\cosh^2\alpha_1 - \cos^2\beta_1}\sinh\frac{\alpha_1 x}{2a}\cos\frac{\beta_1 x}{2a} \\ & \left.-a\,\frac{\frac{1}{2}\sin 2\beta_1 - 2.2\beta_1}{\cosh^2\alpha_1 - \cos^2\beta_1}\cosh\frac{\alpha_1 x}{2a}\sin\frac{\beta_1 x}{2a}\right\} \\ & +L_1\sin\frac{\alpha_1 y}{2a}\sinh\frac{\beta_1 y}{2a}\left\{x\sinh\frac{\alpha_1 x}{2a}\sin\frac{\beta_1 x}{2a}\right. \\ & -a\,\frac{\frac{1}{2}\sinh 2\alpha_1 - 2.2\alpha_1}{\cosh^2\alpha_1 - \cos^2\beta_1}\cosh\frac{\alpha_1 x}{2a}\sin\frac{\beta_1 x}{2a} \\ & \left.+a\,\frac{\frac{1}{2}\sin 2\beta_1 - 2.2\beta_1}{\cosh^2\alpha_1 - \cos^2\beta_1}\sinh\frac{\alpha_1 x}{2a}\cos\frac{\beta_1 x}{2a}\right\} \\ & -M_1\sin\frac{\alpha_1 y}{2a}\sinh\frac{\beta_1 y}{2a}\Gamma(x) + M_1\cos\frac{\alpha_1 y}{2a}\cosh\frac{\beta_1 y}{2a}\Delta(x)\Big], \end{aligned} \tag{9}$$

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where $\Gamma(x)$ = first expression in brackets { },

$\Delta(x)$ = second expression in brackets { }.

$$\frac{\widehat{xy}}{\mu} = \Sigma\Big[L_1 \cos\frac{\alpha_1 y}{2a}\cosh\frac{\beta_1 y}{2a}\Big\{\frac{x}{a}\alpha_1\sinh\frac{\alpha_1 x}{2a}\cos\frac{\beta_1 x}{2a} - \frac{x}{a}\beta_1\cosh\frac{\alpha_1 x}{2a}\sin\frac{\beta_1 x}{2a}$$

$$+(1-\cosh\alpha_1\cos\beta_1)\cosh\frac{\alpha_1 x}{2a}\cos\frac{\beta_1 x}{2a} + \sinh\alpha_1\sin\beta_1\sinh\frac{\alpha_1 x}{2a}\sin\frac{\beta_1 x}{2a}\Big\}$$

$$+ L_1\sin\frac{\alpha_1 y}{2a}\sinh\frac{\beta_1 y}{2a}\Big\{\frac{x}{a}\alpha_1\cosh\frac{\alpha_1 x}{2a}\sin\frac{\beta_1 x}{2a} + \frac{x}{a}\beta_1\sinh\frac{\alpha_1 x}{2a}\cos\frac{\beta_1 x}{2a}$$

$$+(1-\cosh\alpha_1\cos\beta_1)\sinh\frac{\alpha_1 x}{2a}\sin\frac{\beta_1 x}{2a} - \sinh\alpha_1\sin\beta_1\cosh\frac{\alpha_1 x}{2a}\cos\frac{\beta_1 x}{2a}\Big\}$$

$$- M_1\sin\frac{\alpha_1 y}{2a}\sinh\frac{\beta_1 y}{2a}\mathrm{E}(x) + M_1\cos\frac{\alpha_1 y}{2a}\cosh\frac{\beta_1 y}{2a}\mathrm{Z}(x)\Big],$$

where $\mathrm{E}(x)$ = first expression in brackets { },

$\mathrm{Z}(x)$ = second expression in brackets { }. (10)

(8) and (9) are expressions for u and v which satisfy the equations of elasticity and make $\widehat{xx} = \widehat{xy} = 0$ over the free ends of the contour. For numerical interpretation of these results, u and v were made to have given values at isolated points, thus giving equations for L_1, M_1, ..., and the values of these constants obtained by elimination were substituted in (10), thus giving $\widehat{xy}$ as a determined function of x and y. It was not found feasible to work with more than three roots of the transcendental equation; hence there are the six constants, L_1, M_1, ... M_3, determined. The system finally adopted was to add to $\widehat{xy}$ a parabolic term of the usual form and corresponding terms to u and v; the expression already given for $\widehat{xy}$ is then of a corrective nature. u was made equal to the constant e on the face $y = +b$ at the three points $x = 0$, $x = a/2$, $x = a$, and $v = 0$ at the same three points. As v is identically $= 0$ at $x = 0$, we have an extra condition, which we make $\frac{dv}{dx} = 0$ at $x = 0$. (The symmetry of the equations fixes u and v at the corresponding points on the negative side, and on the face $y = -b$.)

The ordinary parabolic term is

$$\widehat{xy} = \tfrac{3}{2}S_0\left(1-\frac{x^2}{a^2}\right) = \tfrac{3}{2}\mu\frac{e}{b}\left(1-\frac{x^2}{a^2}\right),$$

where e is the displacement of the rigid face. The values of u and v which correspond to this are obtained from the equation

$$\mu\left(\frac{du}{dy}+\frac{dv}{dx}\right) = \tfrac{3}{2}\mu\frac{e}{b}\left(1-\frac{x^2}{a^2}\right),$$

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and are
$$u = \left(\tfrac{3}{2}\frac{y}{b} - \frac{y^3}{4(1+\sigma)a^2b} - \frac{3\sigma}{4(1+\sigma)}\frac{x^2y}{a^2b}\right)e,$$
$$v = \left(\frac{3}{4(1+\sigma)}\frac{y^2x}{a^2b} - \frac{\sigma+2}{4(1+\sigma)}\frac{x^3}{a^2b}\right)e.$$

This solution makes $\widehat{xx} = 0$ identically everywhere. We have also for the root $\alpha = 0$, $\beta = 0$, a term
$$u = -L_0\frac{2y}{1+\sigma}, \qquad v = L_0\frac{2x}{1+\sigma},$$
where L_0 can be chosen at pleasure.

Hence, if Σ denote the sum for the first three roots other than zero, putting in the values
$$a = 20, \quad y = b = 5, \quad \sigma = 0{\cdot}25, \quad \text{and} \quad L_0 = 0{\cdot}05e,$$
we have
$$u = -0{\cdot}4e + \left(1{\cdot}4875 - \frac{3}{8000}x^2\right)e$$
$$+ \Sigma\Big[L_1 \sin\tfrac{\alpha_1}{8}\cosh\tfrac{\beta_1}{8}\Phi_1(x) - L_1\cos\tfrac{\alpha_1}{8}\sinh\tfrac{\beta_1}{8}\Psi_1(x)$$
$$+ M_1\cos\tfrac{\alpha_1}{8}\sinh\tfrac{\beta_1}{8}\Phi_1(x) + M_1\sin\tfrac{\alpha_1}{8}\cosh\tfrac{\beta_1}{8}\Psi_1(x)\Big], \qquad (11)$$
$$v = 0{\cdot}08ex + \left(\frac{3}{400}x - \frac{9}{40000}x^3\right)e$$
$$+ \Sigma\Big[L_1\cos\tfrac{\alpha_1}{8}\cosh\tfrac{\beta_1}{8}\Gamma(x) + L_1\sin\tfrac{\alpha_1}{8}\sinh\tfrac{\beta_1}{8}\Delta(x)$$
$$- M_1\sin\tfrac{\alpha_1}{8}\sinh\tfrac{\beta_1}{8}\Gamma(x) + M_1\cos\tfrac{\alpha_1}{8}\cosh\tfrac{\beta_1}{8}\Delta(x)\Big]. \qquad (12)$$

To find the roots of the equation $\sinh 2na = 2na$ (4), we have, putting $2na = \alpha + i\beta$, the two equations
$$\cosh\alpha\sin\beta = \beta, \quad (13) \qquad \sinh\alpha\cos\beta = \alpha. \quad (14)$$

If $\alpha + i\beta$ is a solution of (4), so also are $\alpha - i\beta$, $-\alpha + i\beta$, $-\alpha - i\beta$, but these do not lead to any new expressions for typical terms in u and v. The approximate expressions given by Filon* for the roots of large modulus are not here applicable, as for the first three roots these expressions are very rough, giving values differing from the true ones by from 5 to 1 per cent. for β.

The distribution of the roots is seen by considering the intersections of the curves
$$\frac{\sin\beta}{\beta} = \operatorname{sech}\alpha, \quad (13a) \qquad \cos\beta = \frac{\alpha}{\sinh\alpha}. \quad (14a)$$

* 'Lond. Math. Soc. Proc.,' *loc. cit.*

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(13a) consists of a double branch between $\beta = \pm\pi$, with a node at the origin; as α increases positively or negatively, there are two symmetrical values of β approaching $\pm\pi$. There are no values of β between π and 2π, 3π and 4π, etc.; between 2π and 3π we have two **U**-shaped branches, the distance, d, between the two branches being $> \cosh^{-1}(2\pi)$. Between 4π and 5π, 6π and 7π, etc., we have a series of **U**-shaped branches, the distance d between corresponding branches always increasing as we recede from the α-axis. The diagram is repeated for negative values of β.

(14a) gives between $\beta = \pm\frac{1}{2}\pi$ a curve with two branches, having a node at the origin and asymptotic to $\beta = \pm\frac{1}{2}\pi$. Between $\frac{1}{2}\pi$ and $\frac{3}{2}\pi$, $\frac{5}{2}\pi$ and $\frac{7}{2}\pi$, etc., the curve does not exist; between $\frac{3}{2}\pi$ and $\frac{5}{2}\pi$, $\frac{7}{2}\pi$ and $\frac{9}{2}\pi$, etc., the branches between $\beta = \pm\frac{1}{2}\pi$ are repeated, and similarly for negative values of β.

Inspection of the curves shows at once that there is no intersection, except at the origin, between $\beta = \pm 2\pi$, and that the roots between $\beta = 2\pi$ and $\frac{5}{2}\pi$ are those of least modulus, the modulus of succeeding roots always increasing as we pass out from the origin.

The values of α and β for the first three roots were therefore found as those of smallest modulus. After having obtained approximate values by trial and error, final corrections were made from the following formulæ, given by simple expansion. If $\alpha = \alpha_0 + \eta$, $\beta = \beta_0 + \zeta$, where η and ζ are small,

$$e^{\alpha_0} + e^{-\alpha_0} - \frac{2\beta_0}{\sin\beta_0} = 2\zeta\frac{1-\beta_0\cot\beta_0}{\sin\beta_0} - \eta\,(e^{\alpha_0} - e^{-\alpha_0}),$$

$$\cos\beta_0 = \zeta\sin\beta_0 + \frac{2\alpha_0}{e^{\alpha_0} - e^{-\alpha_0}} + \eta\frac{1-\alpha_0\coth\alpha_0}{\sinh\alpha_0}.$$

The following are the values of the roots:—

Roots of the equation $\sinh(\alpha + i\beta) = \alpha + i\beta$.

$(\pm)\,\alpha_1 = 2{\cdot}768678,$	$(\pm)\,\beta_1 = 7{\cdot}497676,$
$(\pm)\,\alpha_2 = 3{\cdot}352210,$	$(\pm)\,\beta_2 = 13{\cdot}899960,$
$(\pm)\,\alpha_3 = 3{\cdot}716768,$	$(\pm)\,\beta_3 = 20{\cdot}238518.$

The functions $\Phi(x)$, $\Psi(x)$, $\Gamma(x)$, $\Delta(x)$, were calculated for $x = 0$, $x = \frac{1}{2}a = 10$, $x = a = 20$, and $\frac{d\Gamma(x)}{dx}$, $\frac{d\Delta(x)}{dx}$ for $x = 0$. The hyperbolic functions were built up from e^x and e^{-x}, which were worked out by logarithms. The complete expressions for u and v were then computed, and the expressions for u at the three points equated to e, the expressions for v at $x = \frac{1}{2}a$ and $x = a$, and for dv/dx at $x = 0$ equated to zero. From these six equations the constants L_1, M_1, ... M_3 were then obtained by elimination, the laborious arithmetic being done on a "Brunsviga" machine. The functions $E(x)$,

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$Z(x)$, having been evaluated for various values of x, curves of $\widehat{xy}$ along the sections $y = 0$, $y = \frac{1}{2}a$, were plotted: they are shown in fig. 5.

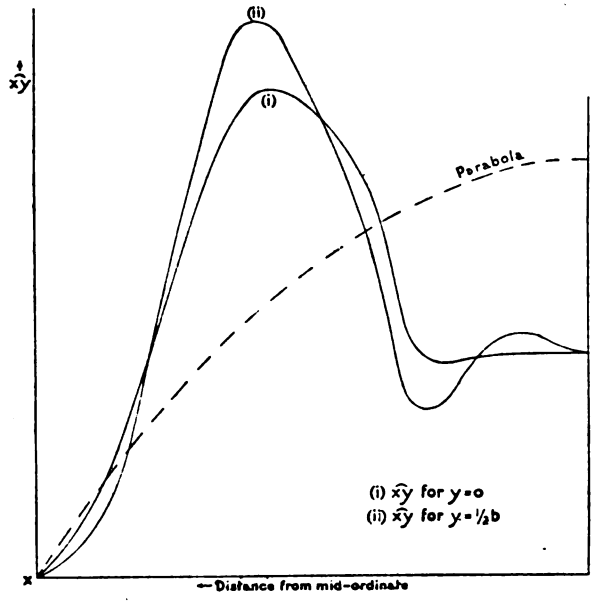

FIG. 5.

As will be seen, they show very markedly the double-headed character found experimentally, but otherwise they do not correspond very closely to experiment. The maxima are more pronounced, and, although the secondary maxima experimentally indicated are shown in Curve ii, the relative magnitudes of the primary and secondary maxima differ rather from the experimental case. The imperfect correspondence may be due partly to weakness of the analytical treatment, partly to the fact that the experimental and analytically assumed conditions are not identical. In the analytical solution we assume the mean value of $\widehat{zz}$ to be zero, and if we integrate the expression for $\widehat{zz}$, we have

$$w_1 - w_2 = -\frac{\lambda}{\lambda + 2\mu}\left(\frac{du}{dx} + \frac{dv}{dy}\right),$$

where w_1, w_2, are the perpendicular shifts at the plane faces considered, and u, v, are the mean shifts in the plane faces. This can, of course, be satisfied at the free faces, but it is not consistent with the constraint at the faces $y = \pm b$, where we must have $w_2 = w_1 = 0$, but $\left(\frac{du}{dx} + \frac{dv}{dy}\right)$ does not vanish. There seems no experimental possibility of giving freedom to the face shifts on the terminal planes $y = \pm b$.

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Again in the analysis no general form of expansion has been obtained, and it seems possible that one condition (say $\widehat{xx} = 0$) may completely determine *all* the constants. Filon* seems to suggest that one such condition accounts for the coefficients corresponding to all the roots of the transcendental equation, and although in this case, if we take the $2m$ constants up to L_m, M_m, we can make the first $2m$ terms of the expansion agree with each one condition at m points, this is forcing the expansion to satisfy an unnatural condition. The divergencies at points other than those selected for restraint will then probably become worse and worse as we take more points, instead of, as we hoped, becoming less. The arithmetic carried out in attempting to put into numbers forms of solution other than those given here† seemed unfortunately to lend colour to this view.

In a paper published when the above work was nearly completed‡ L. F. Richardson has obtained by finite differences an arithmetical solution of the distribution of shear over the base of a dam of complicated contour. The double maximum is indicated, but the maxima are caused by the sharp corners where the dam joins the base, where theoretically the shear is infinite. Within the base of the dam he gives a distribution of shear falling steadily to a minimum at about a quarter span, which differs from most previous experimental work. The boundary taken offers, of course, little resemblance to that here treated.

Summary of Results.

The main results of the work are embodied in the following summary:—

(1) The parabolic distribution hitherto assumed does not give even an approximately correct representation.

(2) Both experimentally and theoretically the distribution of shear is given by a curve having two maxima at about one-sixth span from the end and a minimum at the mid-point. For practical purposes a shear of twice the mean shear at about one-sixth and five-sixths of the breadth at the mid-

* 'Lond. Math. Soc. Proc.,' *loc. cit.*

† A solution was obtained making $u = e$, $v = 0$, everywhere along the rigid faces, but leaving $\widehat{xx}$, $\widehat{xy}$, undetermined at $x = \pm a$. Equations making $\widehat{xx} = \widehat{xy} = 0$ at isolated points gave the constants, and $\widehat{xy}$ was then plotted for different sections. But the curves gave unequal areas for $\int_{-a}^{a} \widehat{xy} \, . \, dx$ over the different sections, showing that there must have been large shears on the free faces between the points at which they were fixed to be zero.

‡ L. F. Richardson, "The Approximate Arithmetical Solution by Finite Differences of Physical Problems, etc.," 'Phil. Trans.,' 1910, A 467. (For the curves referred to, see p. 349.)

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section may probably be taken as the safe limit to maximum shear in the case of blocks of approximately the present ratio of length and breadth.

(3) Secondary maxima are indicated both experimentally and analytically. Such secondary maxima in the shear across the base of their dam are indicated in the work of Pearson and Pollard already referred to.

(4) The failure of the parabolic distribution of shear, which involves and is involved by the linear distribution of normal stresses, shows how inadequate the ordinary engineering theory of both dams and abutments is to meet the requirements, experimental as well as theoretical, of the science of elasticity.

(5) While solutions in functions depending on the roots n of the transcendental equation $\sinh 2na = 2na$ can be made to yield numerical results in some degree corresponding with experiment, it seems at present doubtful whether they are adapted to give a complete and satisfactory solution of the problem when both $\widehat{xx}$ and $\widehat{xy}$ must have known values over two opposite faces.

The work was carried out in the Department of Applied Mathematics of University College, London, at the suggestion of Prof. Karl Pearson, F.R.S., for whose interest, encouragement, and constant assistance the author returns his warmest thanks.

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The Pupil of an Optical System with regard to Perspective.

By Conrad Beck.

(Communicated by Silvanus P. Thompson, F.R.S. Received June 2, 1911.)

Hitherto the use made of the so-called "entrance and exit pupil" of an optical system has been chiefly in regard to aperture and the questions which are related thereto. I have been led to investigate this conception more completely, and I have now found that it may be used with advantage as an additional factor, in connection with the Gauss planes, for explaining the action of optical instruments as regards the perspective of the images formed. The Gauss planes enable us to refer the action of a complicated optical system to an equivalent single lens placed in two positions—the entrance equivalent plane and the exit equivalent plane. In fig. 1, the upper half of the diagram shows the course of a ray of light from X passing through the

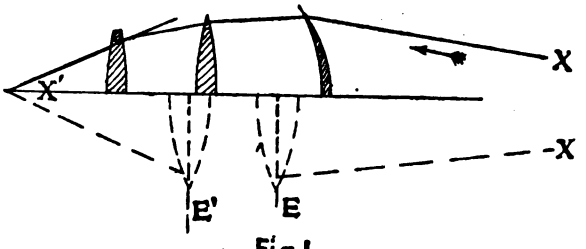

Fig.1

three lenses to X′, each lens bending the light to a certain extent. The lower half of the diagram shows a lens of the correct equivalent focus placed at E to receive the light, and at E′ to discharge it. This will act in a similar manner to the complete system, and many of the properties of the optical system may be correctly studied by confining our attention to an equivalent single lens, placed in the plane E to receive the light, and shifted to the plane E′ to discharge it.

By this means, assuming that the optical system is corrected in such a manner that the oblique rays and those far from the axis act in the same manner as the direct axial rays, the position and size of images can be determined with accuracy; but the perspective of the image cannot be correctly explained by aid of the Gauss planes alone. The "pupils" used as a modifying factor in connection with the Gauss planes will explain this apparent discrepancy.

The conception of the entrance and exit pupils was first emphasised by

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Prof. Abbé. The matter has since been discussed in Germany under the title, "the regulation of the rays." The pupils have, however, been treated as though they were in a certain sense antagonistic to the Gauss planes, and their properties do not seem to have been thoroughly worked out.

The entrance and exit pupils are the equivalent apertures of the optical system, and their service is therefore analogous to that of the equivalent planes and equivalent foci of the Gauss system. By assigning the correct position to these two apertures or pupils we can investigate the perspective of an image without taking further consideration of the system itself; just as by assigning the correct position to the two Gauss planes we can investigate the size and position of the images irrespective of the system itself.

The Gauss equivalent lens tells us the size and position of the image formed. The "pupils" determine what rays form the image, and they further determine the perspective, without invalidating the results given by the Gauss system as to the positions and sizes of the focussed images.

Fig. 2 shows a pair of entrance and exit pupils in the simple case of a single lens with a limiting aperture or diaphragm, D, in front of the lens, L.

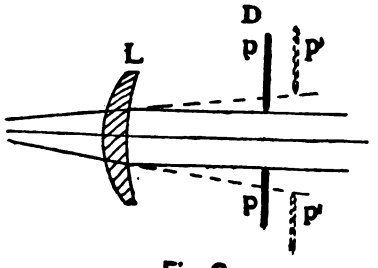

Fig. 2

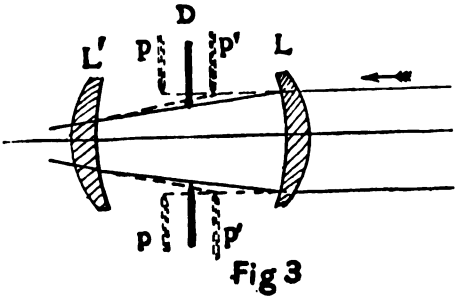

Fig 3

The entrance pupil is, in this case, the actual diaphragm D, but the rays emerge from the lens as if they came from the exit pupil $p'p'$, which is the conjugate image of the stop D seen through the lens L. Whatever may occur to the light before entering or within the optical system, it emerges as coming from the exit pupil $p'p'$.

Fig. 3 shows a pair of lenses, each similar to that in fig. 2, with a limiting aperture D between them.

Here the entrance pupil pp is the conjugate image of the diaphragm D through lens L, and the exit pupil $p'p'$ is, as before, the conjugate image of the diaphragm D through the lens L'. The rays which enter towards the entrance pupils pp emerge as if coming from the exit pupil $p'p'$.

Fig. 4 shows an optical system such as a telephotographic lens, in which the entrance pupil pp and exit pupil $p'p'$ are situated in widely different

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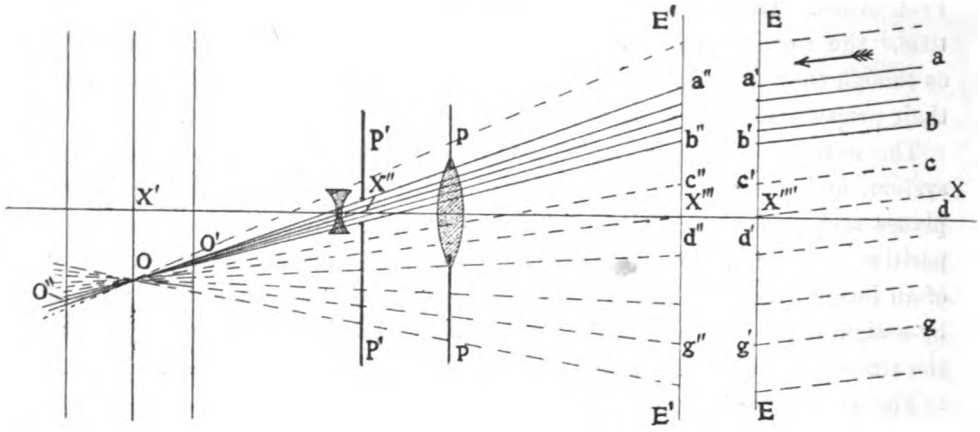

Fig 4

positions from the Gauss equivalent planes EE′. In this case the entrance pupil is situated on the front lens of the system at *pp*, whilst the entrance equivalent plane is at EE, the exit pupil at *p′p′*, whilst the exit equivalent plane is at E′E′.

Fig. 5 shows a lens system of a similar focal length where the exit pupil *p′p′* is in the same position as the exit equivalent plane. A comparison between the two figs. 4 and 5 will demonstrate the effect caused by the exit pupil being displaced in position from that of the equivalent plane.

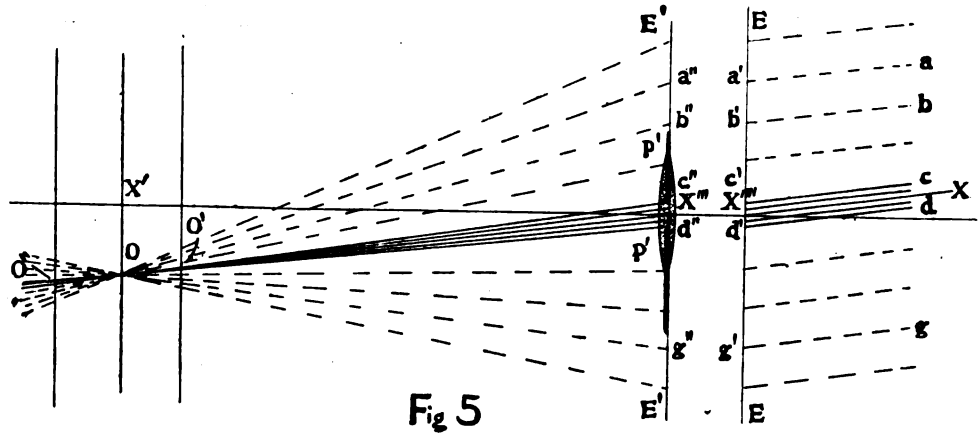

Fig 5

As regards the image of objects to the right of the optical system which are exactly and correctly focussed to any one plane, OX′, to the left of the system, there is no difference—the position and size of the image is the same in both figs. 4 and 5.

One is accustomed to treat optical systems, when using the Gauss planes

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for purposes of finding the size and position of images, as though a pinhole might be placed in the point where the back equivalent plane E'E', fig. 5, cuts the axis at X'''; and lines representing single refracted light rays are drawn from this point into the image-space parallel to incident rays which enter the system towards X''''. The point X''' becomes a projection centre for the system, and its position governs the size and position of images. It would appear at first sight that by displacing the exit pupil, as shown in fig. 4, to a distance from the back equivalent plane, this exit pupil X'', fig. 4, becomes the projection centre and the place at which the pinhole should be placed. It has been further stated that this point forms a geometric centre of projection, regulating the perspective, and that the Gauss system cannot be applied to this class of lens. I shall now show that this is not the case.

It may be assumed for argument that in both cases the optical system is large enough, if the limiting apertures be removed, to admit of the large homocentric bundle of rays *abcdg*. These rays in figs. 4 and 5 encounter the entrance equivalent plane at $a'b'c'd'g'$, and are refracted as coming from points $a''b''c''d''g''$ on the exit equivalent plane. The distance $X''''a'$ equals $X'''a''$, and so on. The rays meet at a point O on the conjugate focal plane X'O. The size and position of the image is in both cases (figs. 4 and 5) the same, being regulated only by the equivalent focal length of the lens, and the positions of the Gauss equivalent planes; but in fig. 4 a limiting or selecting aperture, the exit pupil $p'p'$, has been introduced. It selects a small oblique bundle of rays $a''b''$ out of the homocentric bundle $a''g''$ to form the image; while in the case shown in fig. 5, the limiting aperture $p'p'$ being placed in the exit equivalent plane, the central homocentric portion $c''d''$ forms the image.

The exit pupil is a selecting device which, if situated at any position not coinciding with the exit equivalent plane, admits light which is not a homocentric bundle, but which may always be considered as a portion of the large imaginary homocentric bundle which, if the system had been large enough, would have been transmitted. This conception of treating the oblique bundle of rays by which the image is actually formed as though it were a portion of a large homocentric bundle obeying the ordinary laws of the Gauss method of treatment, obviates the erroneous results previously alluded to.

The perspective of a photograph taken with an optical system as depicted in fig. 4 or fig. 5 does not depend upon the qualities of the image which is in theoretically exact focus on the plane X'O. Only one plane in the object-space corresponds to this one exact plane in the image-space, and objects situated in one plane can have no perspective. Perspective deals with the

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relative positions of points in the image of objects which are at different distances; in fact with the position of objects which are theoretically out of focus, though they may be depicted sufficiently sharply to be well defined in the image. In order to investigate, therefore, the perspective of an image, we must consider the positions of the small out-of-focus circles of confusion which are the images at the plane X′O, of objects that are not in the same plane as the correctly focussed object. It is here that the difference arises between the image of the two optical systems shown in figs. 4 and 5. In the case of fig. 5 the circles of confusion that will be photographed on the point O will be the images of all objects in the object space which are sharply focussed in the image space at their various distances along the line OX‴. In the case of fig. 4 they will be the images of all objects in the object-space that are sharply focussed in the image-space along the line OX″, and not those focussed along the line OX‴. Thus the out-of-focus objects, situated at different distances, which are photographed at one point on the photograph, are different in the two cases, and the perspective will not be the same.

In the case of fig. 5 the line OX‴ is conjugate to a parallel line X⁗X, and all objects lying in the line X⁗X will be focussed on points lying in the line OX‴. Their circles of confusion will lie symmetrically along this line. The photograph is a true projection from the Gauss planes EE′, and the perspective of the picture is such that if a photograph be taken and viewed by an eye placed at E′, it will give the same perspective rendering as that of the object seen from E.

In the case of a system such as fig. 4, however, the objects which have their images situated on the line OX″ do not all lie on a line in the object-space parallel to OX″, but on another line whose position depends on the position of the exit pupil $p'p'$.

A convenient method of expressing the perspective of a photograph is by defining the distance from the eye at which it should be held in order to give on the retina an image in which the proportions of the parts are in the same perspective as is seen by the eye at the standpoint from which the object was photographed, that is, to define the position of the projection centre of the photograph.

In the case of fig. 5 this distance is evidently E′X′—every straight line through the point X‴ (where the back equivalent plane cuts the axis), which defines the centres of circles of confusion of images which are pictured at any point such as O, is conjugate to a straight line parallel to itself with origin X⁗; and the point X‴ is the projection centre of the photograph corresponding to the projection centre X⁗ of the object, because every line in the image-space which passes through the point X‴ has a conjugate line

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parallel to itself which passes through the point X''''. In cases, however, where the exit pupil does not correspond with the equivalent planes, it will be found that the lines on which the circles of confusion lie in the image-space are not parallel to their conjugate lines in the space.

The position of these conjugate lines can be found by reference to fig. 6. The line conjugate to any line OX'', fig. 6, which passes through the centre of

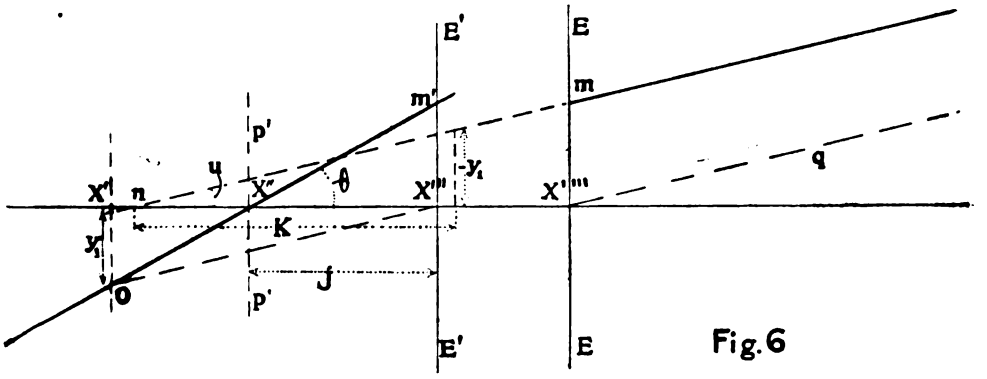

Fig. 6

the exit pupil p' is also a straight line, for let EE and E'E' be the equivalent planes of a system with exit pupil p', take E' as origin for line OX''m', and then call

$$\frac{j}{X'''m'} = \frac{1}{\tan\theta} = b,$$

and the equation for the line OX''m' will be

$$x - by - j = 0. \qquad (1)$$

If we insert in this equation for x and y their values in x' and y', their conjugate points, from the ordinary optical formula, E being the origin for co-ordinates y' and x',

$$x = \frac{x'\phi}{\phi - x'}, \qquad y = y'\frac{x}{x'},$$

we get

$$\frac{x'\phi}{\phi - x'} - by'\frac{\phi}{\phi - x'} - j = 0,$$

or

$$x'\left(1 + \frac{j}{\phi}\right) - by' - j = 0. \qquad (2)$$

This gives the formula for the line nm containing the points conjugate to points on the line OX''m', and it is obviously a straight line. In the case where $y' = 0$

$$x' = \frac{\phi j}{\phi + j}. \qquad (3)$$

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Therefore the line nm cuts the axis at a point $\phi j/(\phi+j)$ from the equivalent plane E.

Where $x' = 0$,

$$y' = \frac{j}{b} = X''''m = X'''m', \tag{4}$$

and it enters the foremost equivalent plane at m, the same distance from the axis as it emerges from the second equivalent plane at m', which is what would be expected.

The distance (K) at which a photograph must be viewed to give the same perspective as that seen from the same standpoint by the eye may be expressed as follows. Let θ be the angle which the line $OX''m'$ makes with the axis, and let u be the angle which its conjugate line nm makes with the axis. The photograph which has superposed on it at the point O all the images which lie along the line OX'' must be viewed at such a distance that it subtends to the eye the angle u such that the distance $K = \frac{y}{\tan u}$.

Now $y = (x-j)\tan\theta$; thus $K = (x-j)\frac{\tan\theta}{\tan u}$,

$$\tan\theta = \frac{X''''m}{j}, \quad \text{and} \quad \tan u = \frac{X''''m}{nX''''} = \frac{X''''m}{x'}.$$

In this case, where $y' = 0$, $x' = \frac{\phi j}{\phi+j}$ from (3);

thus $$\frac{\tan\theta}{\tan u} = \frac{\phi}{\phi+j}, \quad \text{and} \quad K = (x-j)\frac{\phi}{\phi+j}. \tag{5}$$

If $x = -\phi$, $K = -\phi$. But when x is greater than ϕ numerically, K becomes greater than x.

From these formulæ a very simple geometrical construction can be made for showing the position, in the object-space of an optical system, of a line which is conjugate to any given line in the image-space. Suppose that in fig. 6 X'O is the focal plane of the system; from O draw a line OX''' to the back equivalent point, and from X'''' draw a line to $X''''q$ parallel to OX'''. From a point on the first equivalent plane m, where $X''''m = X'''m'$, draw a line parallel to $X''''q$, and this line will be the conjugate line to $OX''m'$. All points which lie along the line nm will have their images on the line $OX''m'$; for from equation (4) where $x' = 0$, $y' = X''''m$, and K for the focal plane $= OX'/\tan u$. In this case (the focal plane) $-K = -\phi$. Thus $-\phi = OX'/\tan u$; also $-\phi = OX'/X'X'''O$. Therefore the angle $OX'''X'$ = the angle u, which proves that the conjugate line nm is parallel to a line drawn to the equivalent point X''' from the point O, where the given line $OX''M'$ cuts the focal plane. The value of K (formula 5) gives

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the perspective centre in terms of the focal length, the position of the photographic plate, and the position of the exit pupil. It also shows that for distant objects sharply focussed where $x = -\phi$, $K = -\phi$, and the perspective centre is in the exit Gauss plane at E′, as would be the case when the exit pupil coincides with the exit equivalent plane; but the case is different for near objects, and an anomalous perspective is produced, which is very unexpected.

To take an example: suppose the equivalent focal length of the system (fig. 4) be 9 inches, and the exit pupil is displaced 5·83 inches behind the equivalent plane, then if a photograph of a distant view be taken, the photographic plate being placed in the focal plane, the perspective will be normal for objects nearly at infinity, and exactly like that taken by any other form of 9-inch lens. Hence, to obtain correct perspective, the photograph must be viewed with the eye at a distance away of 9 inches ($K = \phi$), and not, as has been previously suggested, with the eye at the position of the exit pupil, which in the case chosen is at a distance of 3·17 inches. Were the latter the case, no difference in perspective would be gained by the use of a telephoto lens over a short-focus instrument. If a near object is being photographed, and the plate be placed 18 inches away from the exit equivalent plane, so as to photograph objects full size, the result is remarkable, as in this case $K = 35\frac{1}{2}$ inches, and the perspective centre, instead of being 18 inches away, as would be the case with an ordinary lens, or being 12·17 inches away if the exit pupil were the projective centre, is $35\frac{1}{2}$ inches away, and the perspective is greatly reduced by the use of such a lens.

If the object is photographed half-size, the perspective centre is 22 inches, instead of $13\frac{1}{2}$ inches. This explains a very interesting point in the practical use of telephotographic lenses. Such lenses have usually very small apertures and possess a large degree of so-called depth of focus, and are consequently capable of depicting a great range of depth in the object. For distant views the perspective will, on the whole, give the effect produced by photographing with an ordinary lens of about the same focal length as the equivalent focal length of the telephoto system. But if a telephoto lens be used for near objects, as, for instance, for full-size portraits, the perspective of a 9-inch telephoto lens with exit pupil in the position shown in fig. 4 will give the perspective effect produced by an ordinary lens of $17\frac{1}{2}$ inches focus; or, if half full-size, of a lens $14\frac{1}{2}$ inches. This accounts for the very pleasing portraits obtained by the use of the telephoto lens. For all purposes, except extreme distance, the perspective foreshortening in a photograph taken with a telephoto lens is less pronounced than would be expected from a lens of that focal length.

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I have taken two photographs with two lenses, one the 9-inch telephoto lens described, with exit pupil displaced to about the extent of the example cited, the other with an ordinary photographic lens (see figs. 7 and 8). Both lenses had the same equivalent focal length. The object photographed was a parallel tube, about 5 feet long, built up of laths covered with tissue-paper. The photograph was taken looking down the tube, and the nearest end was in both cases placed at such a distance as to give the same-sized image of the object. It will be noticed that the telephoto lens gives a totally different and less steep perspective effect than the ordinary lens; in fact, the result is more striking than would have been anticipated.

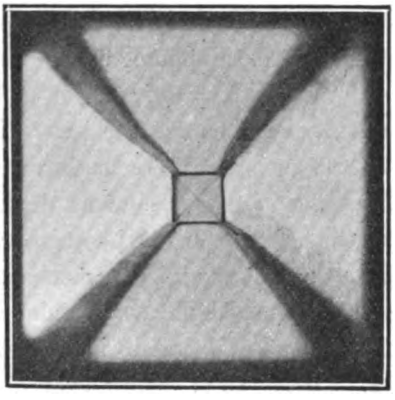

Fig. 7.—Ordinary Lens.

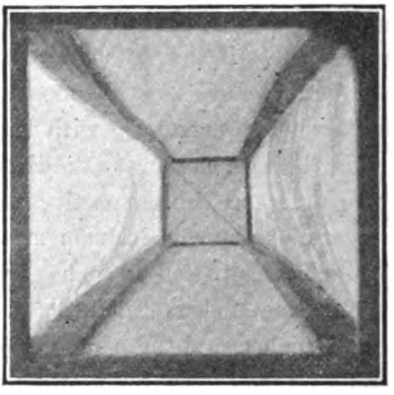

Fig. 8.—Telephoto Lens.

A second pair of photographs, of a row of match-boxes, taken under exactly the same circumstances by the two different types of lenses, shows the same result.

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On Dr. Johnstone Stoney's Logarithmic Law of Atomic Weights.

By Lord Rayleigh, O.M., F.R.S.

(Received July 3, 1911.)

In the year 1888 Dr. G. Johnstone Stoney communicated to the Society a memoir with title nearly as above,* which, however, was not published in full. At the request of the author, who attaches great importance to the memoir, I have recently, by permission of the Council, consulted the original manuscript in the archives of the Society, and I propose to give some extracts, accompanied by a few remarks.

The author commenced by plotting the atomic weights of the elements taken as ordinates against a series of natural numbers as abscissæ. But a curve traced through the points thus determined was found to be "one which has not been studied by mathematicians."

"After many fruitless efforts to extract information from the curves so plotted down, it happily occurred to the author that when we want a geometrical equivalent for atomic weights, they will be even better represented by volumes than by lines. Accordingly a succession of spheres whose volumes are proportional to the atomic weights were taken, and the radii of these spheres were used as the radii vectores of the polar diagram. When this was done, the resulting figure—see Plate III—at once suggested the positive branch of the well-known logarithmic spiral of the second order, viz.:

$$r = \kappa \log (q\theta) \qquad (2),$$

and close scrutiny has fully justified this suspicion. To carry the investigation further, it was found convenient to use rectangular coordinates."

A large part of the paper is occupied with a discussion of the curve plotted to rectangular coordinates in Diagram II from the equation (fol. 6)

$$y_m = \kappa \log (m\alpha) \qquad (3),$$

"where $m = n+r$, (n being successively the several numbers and r for this particular curve being 13); where also $\log \alpha = \bar{1}{\cdot}986$, and $\log \kappa$ [if we use logarithms with 10 as base in equation (3)] $= 0{\cdot}785$."

A referee remarks "there is apparently a slip here: to make the formula agree with the results given as calculated from it, I find it needful to make $\log \alpha = \bar{2}{\cdot}986$, or $\alpha = 0{\cdot}0968$. Written in numerical form, the equation thus becomes

$$y_m = 6{\cdot}096 \log_{10} [0{\cdot}0968\ (n+13)]."$$

* 'Roy. Soc. Proc.,' 1888, vol. 44, p. 115.

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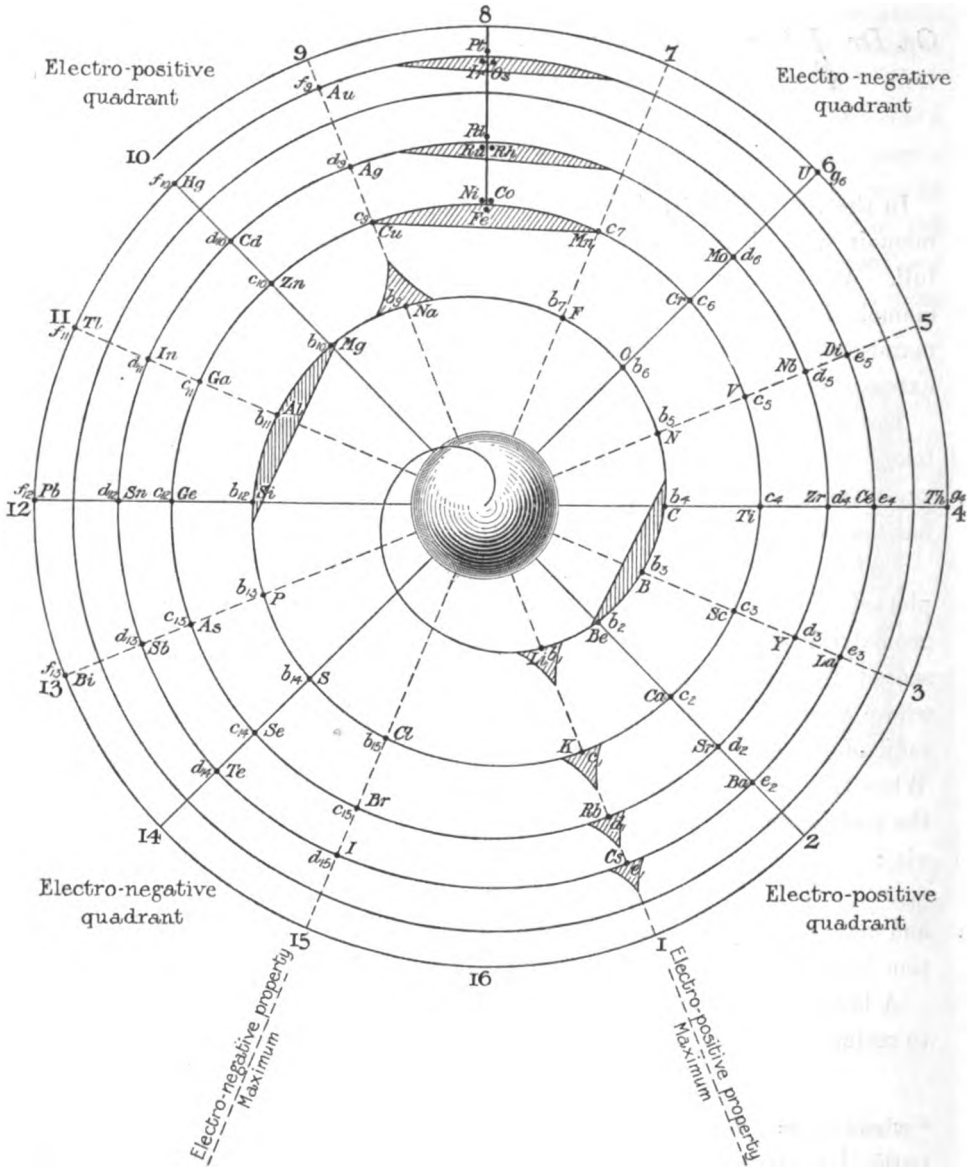

Logarithmic Spiral of the Atomic Spheres.

[Reduced from Plate III of original paper.]

Here n takes in succession the values 1, 2, 3, etc. Subsequently corrections are calculated by which the approximation is still further improved.

What would, I think, be generally regarded as the most important part of the paper is the spiral diagram, subsequently published in 'Phil. Mag.,' September, 1902, and above reproduced from the original drawing:—

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"If in the polar curve

$$r_m = \kappa \log (q\theta_m)$$

we make $q = \frac{8\alpha}{\pi}$ and $\theta_m = \frac{m\pi}{8}$, we obtain a logarithmic spiral presenting in a singularly convenient form the information which a Newlands and Mendeleeff's table can supply, with the addition of also placing before the eye an intelligible representation of the atomic weights. . . . ."

"The quadrants are alternately electro-positive and electro-negative, but while elsewhere the transition between these states is gradual, it becomes abrupt between radius 15 and radius 1. The electro-negative state reaches its maximum in the elements which are ranged along what may be called the sesqui-radius 15, *i.e.* radius 15 along with the inner portion of the opposite radius—radius 7, and is immediately followed upon sesqui-radius 1 by the elements which are in the highest degree electro-positive. This sudden transition may have some connection with the fact that no elements have been found on sesqui-radius 16, although the investigation in § 3 shows that the values of m corresponding to the stations on sesqui-radius 16 cannot be dispensed with."

The vacant places here pointed out are now occupied by the since discovered inert gases. The anticipation is certainly a remarkable one, and it goes far to justify the high claims made for the diagram, as representing in a telling form many of the leading facts of chemistry.

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On Small Longitudinal Material Waves accompanying Light Waves.

By J. H. Poynting, F.R.S.

(Received July 26, 1911.)

All experiments on the pressure of light agree in showing that there is a flow of momentum along the beam. This flow is manifested as a force on matter wherever there is a change of medium. When the light is absorbed, the momentum is absorbed by matter. When the beam is shifted parallel to itself there is a torque on the matter effecting the shift. The momentum would therefore appear to be carried by the matter and not merely by the ether. Though there is an obvious difficulty in accepting this view when the density of the matter is so small as it is in interplanetary space, it appears to be worth while to follow out the consequences of the supposition that the force equivalent to the rate of flow of momentum across a plane perpendicular to a beam of light acts upon the matter bounded by the plane. This rate of flow per square centimetre is equal to the energy density or energy per cubic centimetre in the beam. Of course, in experiments, only the average of the rate of flow during many seconds and the average energy per cubic centimetre in a length of beam of millions of miles is actually measured. But on the electromagnetic theory of light which suggested the experiments and which gives the right value for the pressure, this pressure is equal to the energy density at every point of a single wave.

Let us suppose that we have a train of plane polarised electromagnetic waves of sine form, the magnetic intensity being given by

$$H = H_1 \sin \frac{2\pi}{\lambda}(x - vt),$$

where H_1 is the amplitude of H. The magnetic energy per cubic centimetre at any point is $\mu H^2/8\pi$, and as the electric energy is equal at each point to the magnetic energy, the total energy is $\mu H^2/4\pi$.

The energy per unit volume is $\int_0^1 \frac{\mu H^2}{4\pi} dx = \mu H_1^2/8\pi$.

The pressure p across a transverse surface is

$$p = \mu H^2/4\pi = \frac{\mu H_1^2}{4\pi} \sin^2 \frac{2\pi}{\lambda}(x - vt)$$

$$= \frac{\mu H_1^2}{8\pi} \left\{ 1 - \cos \frac{4\pi}{\lambda}(x - vt) \right\}.$$

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The force on an element of length dx is

$$-\frac{dp}{dx}dx = -\frac{\mu H_1^2}{8\pi}\frac{4\pi}{\lambda}\sin\frac{4\pi}{\lambda}(x-vt)\,dx$$

$$= -\frac{\mu H_1^2}{2\lambda}\sin\frac{4\pi}{\lambda}(x-vt).$$

If ξ is the linear longitudinal displacement of the element there will be a force due to elastic change of volume

$$q\frac{d^2\xi}{dx^2}dx,$$

where q is the elastic constant for compression or extension.

If ρ is the density of the material, the equation of motion is

$$\rho\frac{d^2\xi}{dt} = q\cdot\frac{d^2\xi}{dx^2} - \frac{\mu H_1^2}{2\lambda}\sin\frac{4\pi}{\lambda}(x-vt).$$

Assume $$\xi = A\sin\frac{4\pi}{\lambda}(x-vt-\epsilon).$$

Then, substituting,

$$\left(\rho A\cdot\frac{16\pi^2}{\lambda^2}v^2 - qA\frac{16\pi^2}{\lambda^2}\right)\sin\frac{4\pi}{\lambda}(x-vt-\epsilon) = \frac{\mu H^2}{2\lambda}\sin\frac{4\pi}{\lambda}(x-vt).$$

Putting $x = 0$ and $t = 0$, we see that $\epsilon = 0$. Putting $q = \rho u^2$, where u is the velocity of free elastic waves of the q type, and assuming that the longitudinal waves are forced waves, keeping exact time with the waves of light, we have

$$A = \frac{\lambda\mu H_1^2}{32\pi^2\rho(v^2-u^2)}.$$

As u/v is negligible for all ordinary matter,

$$\xi = \frac{\lambda\mu H_1^2}{32\pi^2\rho v^2}\sin\frac{4\pi}{\lambda}(x-vt)$$

$$\xi = \frac{\mu H_1^2}{8\pi\rho v}\cos\frac{4\pi}{\lambda}(x-vt).$$

The potential energy in these waves is negligible in comparison with the kinetic. We have then

$$\text{Energy per unit volume} = \tfrac{1}{2}\int_0^1\rho\xi^2 dx = \frac{\mu^2 H_1^4}{256\pi^2\rho v^2}.$$

As the electromagnetic energy per unit volume is $\mu H_1^2/8\pi$,

$$\frac{\text{Energy in longitudinal waves}}{\text{Electromagnetic energy}} = \frac{\mu H_1^2}{32\pi\rho v^2} = \frac{1}{8}\frac{\mu H_1^2}{8\pi}\Big/\frac{\rho v^2}{2},$$

which is one-eighth of the electromagnetic energy divided by the energy

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which the matter would have if it were moving with the velocity of light in that matter.

This shows how infinitesimal is the fraction of the energy of the beam which is located in these waves of compression of the material.

The fraction is proportional to the intensity of the beam.

As an example, take a beam of the intensity of full sunlight just outside the earth's atmosphere, in which the energy flow is about $1{\cdot}4 \times 10^6$ ergs/sec. The energy density $\mu H_1^2/8\pi$ is therefore $1{\cdot}4 \times 10^6 \div v$. Put $v = 3 \times 10^{10}/n$, where n is the refractive index. The fraction is

$$\frac{1}{4} \cdot \frac{1{\cdot}4 \times 10^6}{27 \times 10^{30}} \frac{n^3}{\rho}, \text{ or about } 1{\cdot}25 \times 10^{-26} n^3/\rho.$$

At the surface of the sun it would be about 40,000 times as much, say, $5 \times 10^{-22} n^3/\rho$.

It is interesting to note that if a beam of light is incident on any reflecting or absorbing surface and if the pressure of light is periodic with the waves it must give rise to ordinary elastic waves in the material of frequency double that of the light waves.

The Properties of Colloidal Systems.—II. *On Adsorption as Preliminary to Chemical Reaction.*

By W. M. Bayliss, F.R.S., Institute of Physiology, University College, London.

[This paper is published in 'Proceedings,' Series B, vol. 84, pp. 81—98.]

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On the Boiling Point of Water.

By The Earl of Berkeley, F.R.S., and M. P. Appleby, M.A., B.Sc. (Oxon).

(Received March 23, 1911.)

Introduction.—In the course of some work, communicated to the Royal Society* by one of us, in which determinations of the boiling points of some saturated solutions were made by Buchanan's method (the so-called Landsberger-Sakurai method), it was pointed out that these boiling points probably varied according to the height of liquid operated upon. During the course of that research a few experiments, which, however, are not recorded in the paper, were made on the boiling point of water; and it was found that this boiling point was approximately that due to a head of water equal to half the total height of liquid.

The paper cited mentioned the hope that direct osmotic pressure measurements might be obtained; this hope has not been fulfilled, but as an exact connection between the vapour-pressure and the osmotic pressure of a solution has since been worked out,† a knowledge of the boiling points will enable the osmotic pressure to be calculated.

In the same paper it was pointed out that more accurate results might be obtained by means of platinum thermometers, and as a preliminary it was thought advisable to investigate, if possible, the relation between the pure solvent's boiling point and the conditions under which it is being observed.

Apparatus and Method of Determination.—Fig. 1 gives a diagrammatic representation of the electric connections, together with a section through the apparatus in which the boiling points were determined. This vessel, which is shown at A, is thoroughly lagged; water is boiled in the lower part and its vapour is forced through B and through the water in C (the boiling-point vessel proper), to be condensed at D, and the amount condensed measured in the graduated cylinder E. C is graduated, along its vertical axis, in centimetres and half centimetres, and is closed by an india-rubber stopper, through which is passed one of the platinum thermometers T_1. The other thermometer T_2 is placed in the hypsometer F.

The two thermometers were obtained from the Cambridge Scientific Instrument Company, and were placed, as shown, at the ends of the Wheatstone bridge wire. They were furnished with compensating leads, but

* Berkeley, 'Phil. Trans.,' 1904, A, vol. 203.

† Porter, 'Roy. Soc. Proc.,' 1907, A, vol. 79, p. 521.

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these are omitted from the diagram. Each thermometer had a resistance of about 7 ohms at 100° C., and a fundamental interval of 2 ohms.

The bridge,* also made by the Cambridge Instrument Company, was 150 mm. long, and was furnished with a sliding contact moved by a screw with a micrometer head. The position of the contact could be read to 0·01 mm., and, if necessary, estimated to 0·001 mm. The battery and galvanometer circuits were closed by means of a Griffiths reversing key so as to eliminate some of the thermo-currents.

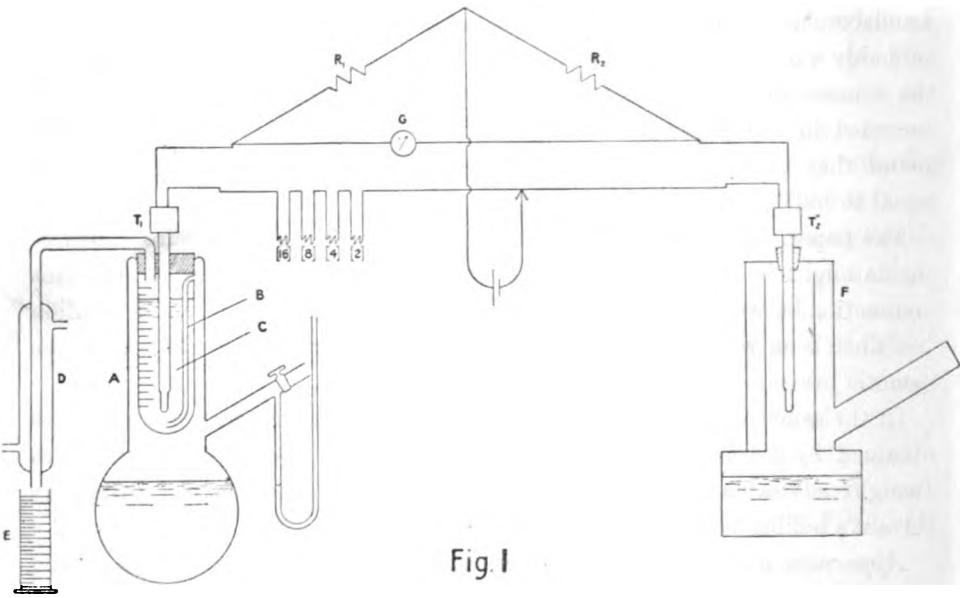

Fig. 1

The bridge wire was very carefully calibrated by the late Mr. A. E. Green, but before using it for this research it was again calibrated by Mr. J. Stephenson.

[2], [4], [8], and [16] were bridge extensions made of manganin, any one of which could be thrown in when the difference of temperature between the two thermometers was larger than could be dealt with on the bridge wire alone; they were only used in the observations on solutions. These extensions were made by Mr. Stephenson and calibrated in terms of the resistance of the mean bridge wire millimetre with the following results:—

* This bridge was designed for another research and is not very suitable for the work here recorded.

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Table I.

Extension.	Resistance in M.B.M.		
[2]	302·84	302·12	302·06
[4]	600·59	600·47	600·49
[8]	1194·77	1194·79	1194·71
[16]	2378·37	2378·47	2378·47

R_1 and R_2 were two coils of very nearly equal resistance of 5 ohms, kindly lent to us by Principal E. H. Griffiths.

The mean resistance of 1 mm. of the bridge wire was 0·000144495 ohm. A movement of 1 mm. in the position of the sliding contact was equivalent to a temperature difference of 0·01445° C.; thus the error in reading the temperature difference between the two thermometers is not more than 0·0001° C.

Determination of the Fixed Points of the Thermometers.—The difference of resistance of the thermometers was found by finding the centre of resistance of the system—thermometer T_1, bridge extensions, bridge proper, thermometer T_2. The fixed points were determined several times by measuring—

(1) The balance-point when both thermometers were in the same hypsometer.

(2) The balance-point when one thermometer was in the hypsometer and the other in ice. For this purpose two standard 1 ohm manganin coils were connected in series with the ice thermometer, the coils being immersed in a stirred oil bath kept at 15° to 16° C.

The results of the observations under the heading (1) are given in Table II:—

Table II.—Hypsometer Point.

Date.	Bridge readings.
1910.	
January 13	84·48
April 18	84·06
May 26	84·06
July 22	83·75
October 3	84·10
„ 28	84·30
November 16	84·25

It will be seen that there are slight variations in the hypsometer point, these variations are in the thermometers themselves,* for the centre of the

* Towards the end of the experiments it was discovered that the thermometers gave the same balance-point if the exposed part of their stems were carefully lagged and if they

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bridge was also tested at intervals and was found not to move by more than 0·07 mm.

The results under heading (2), which gives the fundamental interval, are recorded in Table III :—

Table III.—Fundamental Interval.

Date.	Fundamental interval.	Number of observations.
1910.	ohms.	
January 18.....	1·99985	6
April 18.....	2·00041	1
July 24.....	1·99942	4
October 4.....	1·99993	1

The Boiling Point of Water.—Two advantages accrue through the use of differential platinum thermometers. The compensating leads greatly reduce "emergent column" errors, and by having one of the thermometers always in a hypsometer, the effect of barometer changes on the boiling point of the pure liquid is automatically eliminated.

It was found early in the course of the research that the boiling point was affected not only by the height of water through which the steam had to pass, but also by the rate at which it was passing; and this obtained although the stirring was so thorough that on moving the thermometer to different positions the maximum variation was not more than 0·001° C.

The following table gives the observations on the variation in the boiling point of water :—

Column (1) gives the rate of passage of steam; that is, the number of cubic centimetres of water condensed into E (fig. 1) in 10 minutes.

Column (2) gives the height of water above the orifice of the jet B. This height is tabulated, instead of the total height of the water, for a reason which will be apparent later. The orifice was 5 mm. above the bottom of the vessel C.

Column (3) gives the "observed" difference in temperature between the two thermometers. In the experiments the actual rate of passage of steam was seldom exactly that given in (1). The numbers here tabulated are the observed differences of temperature corrected to the rates in column (1) by means of a factor which was experimentally determined.

were passed through the hypsometer cover to the same depth. Fortunately the hypsometer point was determined before each series of boiling-point observations, and during that series thermometer T_2 was never moved from its position, while T_1 was lagged, so that no error greater than other experimental errors will occur through referring each series to the previous hypsometer-point determination.

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Column (4) gives the difference in temperature calculated from the assumption that the rise is directly proportional to a pressure equivalent to half the head of water recorded in column (2).

Column (5) gives the differences between the numbers in columns (3) and (4).

Column (6) gives the difference in temperature calculated from the constants of a theoretical equation to be developed later.

Table IV.—Results for Water.

(1) Water condensed in 10 minutes.	(2) Height of water above orifice.	(3) Observed rise in temperature.	(4) Rise calculated from half-height assumption.	(5) Differences.	(6) Rise calculated from theory.
c.c.	cm.	° C.	° C.		° C.
8	3·95	0·0272	0·0510	0·0338	0·0253
8	4·8	0·0340	0·0620	0·0280	0·0338
8	4·9	0·0353	0·0634	0·0281	0·0348
8	4·9	0·0348	0·0634	0·0286	0·0348
8	5·0	0·0363	0·0647	0·0284	0·0358
8*	5·65	0·0410	0·0731	0·0321	0·0427
8	6·0	0·0465	0·0776	0·0311	0·0465
8	6·1	0·0484	0·0789	0·0305	0·0476
8*	6·8	0·0517	0·0880	0·0363	0·0554
8	7·6	0·0627	0·0983	0·0356	0·0645
16	3·85	0·0220	0·0498	0·0278	0·0213
16	4·8	0·0299	0·0620	0·0321	0·0300
16	4·85	0·0309	0·0627	0·0318	0·0305
16	4·95	0·0315	0·0640	0·0325	0·0314
16	5·2	0·0344	0·0673	0·0329	0·0339
16	5·2	0·0342	0·0673	0·0321	0·0339
16	5·6	0·0362	0·0724	0·0362	0·0378
16	6·6	0·0481	0·0854	0·0373	0·0481
32	4·8	0·0234	0·0620	0·0386	0·0236
32	5·4	0·0270	0·0698	0·0428	0·0285
32	7·5	0·0500	0·0970	0·0470	0·0475

* There was some uncertainty in the rate of passage of steam in these experiments.

It is at once apparent that the numbers in column (4) fail to represent the facts. And on comparing results for the same height of liquid, but different rates of passage of steam, it is evident that the faster the steam passes the less the rise of temperature. This latter effect is well shown in Table V.

The height of liquid above the orifice in these experiments was in most cases 5 cm., but some of the numbers are intrapolated to that height from the graphs of rise of temperature with height.

The results tabulated in Table IV are plotted in curve (1). It will be seen that the points do not lie on a straight line, but on a curve convex to the axis along which the height of the liquid is measured, but the curves approximate to straight lines as the height of liquid increases.

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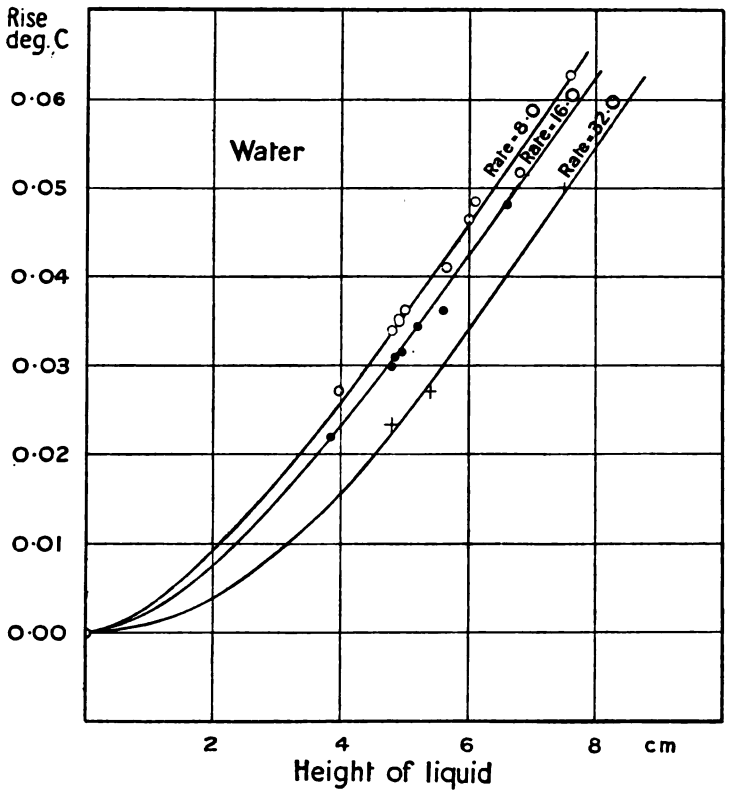
Table V.—Effect of varying the Rate of Steam.

Rate.	Rise in temperature.
	° C.
1·2 c.c. water condensed in 10 mins.	0·0481
6·6 ,, ,, ,, ...	0·0370
8·7 ,, ,, ,, ...	0·0356
9·35 ,, ,, ,, ...	0·0347
14·1 ,, ,, ,, ...	0·0325
15·7 ,, ,, ,, ...	0·0319
15·7 ,, ,, ,, ...	0·0316
16·0 ,, ,, ,, ...	0·0326
18·3 ,, ,, ,, ...	0·0321
32·8 ,, ,, ,, ...	0·0225
32·8 ,, ,, ,, ...	0·0243

Curve 1.



From the nature of the phenomena it is evident that the curve must (in the case of water) pass through the origin, and this point is the temperature of the steam in the hypsometer.

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On drawing the curve it is found that the points lie on a hyperbola, and this hyperbola cuts the axis of temperatures approximately at right angles.

Theory.

Effect of Varying the Height of Liquid (the Rate of Bubbling remaining Constant).—(1) In the following theoretical discussion, we will measure all temperatures, vapour-pressures, and steam pressures (by steam pressures we mean the pressure of the steam in the bubbles or in the free space above the liquid) from the hypsometer point, that is, from the temperature and pressure of the steam in the hypsometer at the moment of observation.* In so far as the temperatures are concerned, the differential arrangement of the platinum thermometers accomplishes this automatically.

Incidentally it may be mentioned that the reasoning is applicable to the equilibrium temperatures of any boiling solution, even when saturated.

(2) The notation used is:—

p = the vapour-pressure of the liquid when in temperature equilibrium.

t = the corresponding temperature.

P = the pressure of the entering steam; obviously this pressure is that due to the total height h of liquid.

T = the temperature corresponding to P, that is, the temperature of boiling water when its vapour-pressure is in equilibrium with steam under the pressure of the atmosphere together with that due to the height h.

P_1 = the mean pressure of the steam in the bubbles during their traverse through the liquid.

T_1 = the mean temperature of the bubbles.

(3) To simplify the argument we will make the following assumptions, which will be dealt with later:—

(*a*) The change in the vapour-pressure of a liquid with change in the hydrostatic pressure upon the latter may be neglected.

(*b*) The hydrostatic adjustment of pressure in the bubbles is practically instantaneous; but, as can be seen by the fact that the bubbles remain in existence at all, the vapour adjustment across the interface only takes place in a time longer than is required for a bubble to traverse the liquid.

* Sakurai ('Chem. Soc. Journ.,' 1892, vol. 61, p. 495) showed that unless special precautions were taken to avoid wetting the thermometer or walls of the vessel in the space above the surface of the liquid, the free steam in that space was always at the hypsometer point.

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(*c*) The bubbles on entering the liquid are all of the same size (see later).

(*d*) The height of the liquid has no appreciable effect on the size of the bubbles as they ascend (see later).

(*e*) The main cause of the adjustment of temperature is the heat of condensation (or evaporation) of steam at the bubble interface and at the free surface. There is, however, a small radiation effect which will be dealt with later.

(4) Consider now the actual apparatus; it is easy to see that if there were no stirring the liquid would be hotter at the bottom than at the top, and would have corresponding vapour-pressures at these levels. Efficient stirring causes the whole mass to take up a temperature and vapour-pressure somewhere intermediate between these extremes, so that the pressure of the entering steam is higher than the vapour-pressure of the liquid, while at the surface the vapour-pressure is higher than the hypsometer steam pressure.*

(5) In the experiments we establish a temperature equilibrium—hence the rate of cooling must equal the rate of heating.

From the construction of the apparatus cooling practically only takes place at the free surface (in the case of solutions, the loss of heat through the walls of the boiling vessel may be appreciable—we discuss this point in the succeeding paper). The rate of cooling will be approximately proportional to the small difference between the vapour-pressure of the liquid and the hypsometer pressure, that is, proportional to p; as this takes place across the free surface, whose area is independent of the height of liquid, we may put the rate of cooling $= bp$, where b is a constant depending on the free surface area.

(6) In a similar manner the rate of heating is proportional to the pressure difference between the mean steam pressure in the rising bubbles and the vapour-pressure of the liquid, that is to $P_1 - p$; it is also proportional to the number of bubbles in the liquid, that is to h. The rate of heating may therefore be put $= ah\,(P_1 - p)$, where a is dependent on the mean bubble area, which, by hypothesis, is constant for the same rate of bubbling, and is independent of the height of liquid.

(7) Equating the rates to one another, we get

$$bp = ah\,(P_1 - p). \qquad (1)$$

* If there were no heat losses the stirred liquid would have a vapour-pressure and temperature exactly midway between the extremes; that is, its vapour-pressure would be $h/2$, while the temperature would be the boiling point of the liquid when under the same pressure. Thus the bubble in the first half of its rise would impart heat to, and in the second half it would receive heat from, the liquid.

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Remembering that $P_1 = k_2 h$, that $p = k_1 t$, and putting $\beta = b/a$, the equation reduces to

$$t = kah^2/(h+\beta), \qquad (2)$$

where k is a new constant.

The form of curve represented by this equation is a hyperbola cutting the axis of temperatures at right angles, at the point where $t = 0$, that is, at the temperature of the steam in the hypsometer.

As a test of this formulation, we have included in Table IV, in column (6), the equilibrium temperatures for different depths of water calculated by means of equation (2) from the respective hypsometer point and one other point on the graph of height against observed rise. On comparing columns (3) and (6), it will be seen that there is a satisfactory agreement between the numbers.

The constants used in the calculation were—

$k = 0{\cdot}0131$, and
$\beta = 4{\cdot}14$ for a rate of condensation of steam of 8 c.c. in 10 mins.
$\beta = 5{\cdot}26$ " " " 16 "
$\beta = 8{\cdot}0$ " " " 32 "

Dealing with the assumptions (*c*) and (*d*) together, the following would seem to justify them. In the drop method of determining surface tension, it is proved that the size of the drop is, for the same orifice, solely a function of the surface tension and the density; similarly, if we neglect the effect of the momentum of the stirred liquid (this is allowable, as it is practically independent of h), the size of the bubble as it leaves the orifice is a function of the surface tension between water and steam, and also of the difference in density between the contents of the bubble and the water it displaces. As neither of these factors vary appreciably, the bubbles may be taken to be, initially, of the same size.

There are, however, three effects to be considered: (1) It is obvious that the bubble expands as it rises through the liquid. Calling its initial volume m_0, its final volume (m) on emerging will be $m = m_0(H+h)/H$ (where H is the barometic height), its mean volume $\bar{m}$ will be $\bar{m} = m_0(1+h/2H)$, and the mean area $\bar{\Sigma}$ will be $\bar{\Sigma} = \Sigma_0(1+h/3H)$. This change in area is negligible.

(2) Although, initially, the bubbles are of the same size, a difference in the height of liquid produces a difference in the pressure of the steam they contain. Using the same symbols, with the suffixes 1 and 2 to refer to different heights h_1 and h_2, it is easy to see that the ratio of the mean areas will be $\bar{\Sigma}_1/\bar{\Sigma}_2 \doteqdot (1+(h_1-h_2)/3H)$. This also is negligible.

(3) The amount of steam condensed in the liquid is so small (maximum

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rate of rise of height equals 1 mm. in one hour) that the consequent change in "bubble" area may also be neglected.

Dealing now with the radiation mentioned in paragraph (*c*); the following seems to fix an upper approximate limit to the effect. On account of the high opacity of water and aqueous solutions to low heat rays, we may assume that the radiation from the liquid is chiefly a surface phenomenon, but with steam, which is more transparent, it will be a volume effect.

There are two radiation interchanges to be considered: (1) the cooling across the free surface of the liquid—the rate at which this cooling takes place is independent of the height, and depends only on t, the effect being small* we may take the rate as proportional to t, and put it equal to bk_0t; (2) the second radiation interchange, which is that between the liquid and the bubbles, is, in the case of water, a heating effect, but in the case of most saturated solutions, where the liquid is hotter than the entering steam, there is a loss of heat; in either case the same function applies. There is little doubt that the bubbles, for the most part, attain a temperature equilibrium with the liquid before they leave it; otherwise when the thermometer is moved about there would be fluctuations in the galvanometer; assuming this,† then, as before, the rate is proportional to the differences between the temperature of the liquid and that of the entering steam T, and we may put it $= \pm v(\mathrm{T}-t)$, where v is a constant depending upon the volume of the bubbles.

Adding these two corrections to equation (1), and remembering that T is proportional to h, it reduces to

$$t = (\mathrm{A}h^2 \pm \mathrm{C}h)/(h+\mathrm{D}). \qquad (3)$$

The constants are altered so as to simplify the equation.

This equation represents a hyperbola, but it no longer cuts the axis of temperatures at right angles. In the next paper, where we deal with the much greater radiation losses in the saturated solutions, the experiments show that even there these losses may be neglected; we may therefore take it that equation (2) represents the observations.

Anomalies Due to Varying the Rate of Bubbling.—The results of varying the rate of passage of steam are given in Table V and plotted in Curve 2. As already stated, it is apparent that an increase in the rate of steam is accompanied by a fall in temperature.‡

This change is, at first sight, somewhat surprising; it would be thought

* This, even in the case of saturated solutions, when $t = 20°$, is shown in the next paper to be so.

† We are here dealing with an upper limit, for it is easy to show that if we assume that the bubbles do not reach temperature equilibrium before they leave the solution, we shall get exactly the same form of equation as in equation (2).

‡ *Cf.* Sakurai, *loc. cit.*

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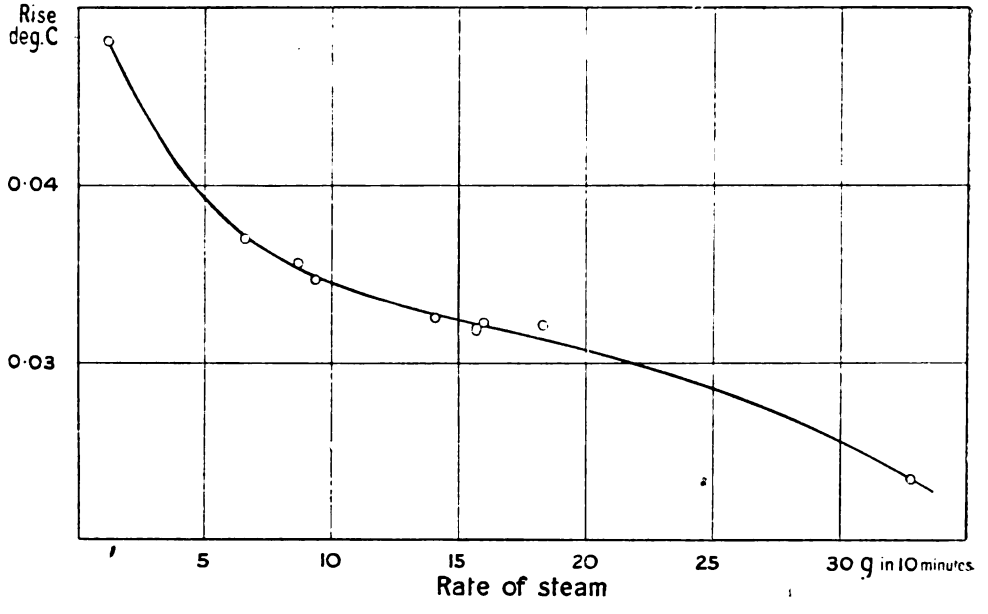
that the area of the steam bubbles in contact with the water at any moment, and therefore the heating effect, would be approximately proportional to the rate at which the steam was supplied.

CURVE 2.



We would offer the following tentative explanation of the apparent paradox:—The area of the steam bubbles in contact with the water at any instant depends not only on the rate at which the steam is supplied, but also on the velocity with which the bubbles pass through the liquid. Now, in the experiments a more or less rapid circulatory motion is always imparted to the water, and, as far as eye observations enabled us to judge, the velocity of circulation was roughly proportional to the rate of supply of steam; consequently, since the whirl of liquid carries the bubbles with it, it follows that their velocity is also proportional to the rate of steam supply, and, further, there was distinct evidence that with the faster rates of bubbling there was a tendency for the bubbles to coalesce, thus reducing the heating surface.

We may take it, therefore, that the factor a in equation (1), instead of increasing with an increase of steam supply, actually diminishes. On the other hand, the rapid passage of bubbles tends to increase the cooling surface by the extension of the free surface on account of agitation, and also by throwing particles of water into the hypsometer space above. Thus the factor b of the equation is increased.

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It will be seen on referring to the values of β given on p. 485 that for an increase of passage of steam from 8 to 16 c.c. in 10 minutes, $\beta(=b/a)$ increases about 20 per cent., an increase which does not seem incompatible with the foregoing discussion. The rate of 32 c.c. in 10 minutes was much too fast for any bubbles to be seen. A further test of equation (1) was made by observing the rise in boiling point in a vessel of a larger diameter. The results are tabulated below :—

Table VI.—Comparison of Vessels of different Diameters.

Height of liquid.	Rate of steam.	Observed rise in vessel of diameter 4·4 cm.	Observed rise in vessel of diameter 5·75 cm.
cm.	c.c. in 10′.	° C.	cm.
5·5	9·1	0·0384	0·0309
5·6	9·2	·0393	·0338
6·7	5·2	·0561	·0477
6·8	7·9	·0532	·0455
7·6	11·5	·0591	·0510
7·8	11·5	·0620	·0540

It will be seen that the increase in the evaporation surface causes a considerable fall in temperature in each experiment. The fall in temperature is only 70 per cent. of that calculated on the assumption that we are dealing with a change of free surface proportional to the change in the cross section of the vessels. We think the discrepancy is sufficiently accounted for when it is remembered that the free surface is a turbulent one, and the form of the vessel and the shape of the steam jet will influence this very considerably. In the wide vessel the jet pointed downwards at an angle of about 45°, while in the small apparatus it was approximately horizontal.*

That the form of the jet has considerable influence on the circulation, and consequently on the free surface, was proved by experiments which need not be detailed here. It was found that in the same vessel, and under the same conditions of bubbling and height, a jet pointed vertically downwards raised the temperature higher than one placed horizontally, both jets having the same diameter.

Conclusions.—The constant temperature at which a liquid boils, as distinguished from the "hypsometer" point, is a function of several factors, among which are the height of liquid, the rate of passage of the vapour bubbles, etc. To get comparable results the observed values must be extrapolated down to a hypothetical value for an infinitely small layer of

* Mr. W. E. S. Turner, 'Journ. Chem. Soc.,' 1910, vol. 97, p. 1184, finds that the rise in the boiling point of chloroform is smaller than that due to a pressure of half the height of the liquid, and that it is smaller the wider the vessel.

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liquid. This temperature will be the "hypsometer" point. As these variable factors are operative in any method of boiling a liquid, heating by a flame or by an electric current will give no better results than the method we used. Here again it is necessary to obtain a series of observations and extrapolate to an infinitely small layer of liquid.

In the case of solutions, the hypsometer point cannot be determined directly, so that we must fall back on determinations of the temperatures of the boiling liquid; these are also variable, and it would seem that a definition of what is meant by the boiling point of a solution is required. We would suggest the following:—Assuming that the solution is under a standard atmospheric pressure of 760 mm. of mercury, then the boiling point is the temperature of a small layer when its vapour is in equilibrium with the free vapour above it.

On the Boiling Points of some Saturated Aqueous Solutions.

By The Earl of Berkeley, F.R.S., and M. P. Appleby, M.A., B.Sc. (Oxon).

(Received March 23, 1911.)

Introduction and General Discussion.—These experiments were made so as to obtain as accurate data as we could for the purpose of calculating the osmotic pressures of the solutions. The method for determining the boiling points was that already detailed in an earlier communication to the Society,* except that differential platinum thermometers were used as described in the paper "On the Boiling Point of Water."

One of the platinum thermometers was always in the hypsometer, and to get the true boiling point as defined in our previous paper the height of the barometer and height of solution were systematically noted. The chief difficulty of the experiments was that of keeping the solutions saturated. It was found necessary to use a large quantity of finely powdered salt, and to keep the solid in rapid motion by a sufficiently powerful current of steam. If large crystals are used, or if the salt has been left in contact with the solution too long at the end of an experiment, so that crystals have grown, the next experiment will give low values for the equilibrium temperature, showing that the solution is not saturated. At times it happened that a paste of crystals was formed, which offered so much resistance that the

* Berkeley, 'Phil. Trans.,' A, 1904, vol. 203.

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steam entered at a pressure greater than normal, thus giving too high a value to the boiling point.

Usually fresh salt was ground up and placed in the apparatus before each determination. The most suitable quantity of salt varies for each substance, but was found by experiment. The rate of passage of steam, as measured in the condenser, was about 3 grm. per minute. The temperature of the solution does not remain constant, but rises continually as the steam condenses, even after saturation is practically reached; this rise is caused by an increase in the height of solution above the orifice, and is quite analogous to the change in boiling point with height of liquid discussed in the preceding paper.

It is evident that the rise due to an increase in depth of liquid will be different for different salts, both because the densities of the saturated solutions are different, and because the solubilities differ, the effect of pressure on the boiling point being greater with the more soluble salts. It was also found that the rate of increase in depth varied with the solubility of the salts.

Particulars of the Salts Used.—Many of the salts were those used in the previous work and recrystallised; these in the following list are marked 1904:—

NaCl. Kahlbaum's purest.

KCl. Merck's "guaranteed."

RbCl. 1904, and a second specimen from Merck which gave higher results, but on the third recrystallisation the results were the same as the 1904.

CsCl. 1904.

TlCl. 1904.

Na_2SO_4. Merck's "guaranteed."

K_2SO_4. Merck's, lower values were obtained after recrystallisation.

Rb_2SO_4. 1904, and some made from Merck's Rb_2CO_3. The whole lot was recrystallised.

Cs_2SO_4. 1904, and some prepared from Merck's Cs_2CO_3. The 1904 sample was accidentally spilled on the bench and contaminated with cyanides; the second contained organic matter. Both were repeatedly recrystallised, and their purity checked by spectroscopic examination.

Tl_2SO_4. 1904.

$NaNO_3$. Kahlbaum's purest.

KNO_3. Kahlbaum's purest.

$CsNO_3$. 1904; also used in a research by Mr. T. R. Merton.* This salt was three times recrystallised before use.

$SrNO_3$. This salt was prepared from the carbonate, and was free from calcium, but it was found to contain a small proportion of barium nitrate. It was freed from the latter salt by dissolving in water and throwing it out of solution by means of alcohol and ether; this process was repeated till no trace of barium could be found on the addition of potassium chromate. It was then repeatedly recrystallised from water. No impurities could be detected in the resulting product.

* 'Journ. Chem. Soc.,' 1910, vol. 97, p. 2454.

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Examples of the Observations.—The following two examples are extracted from the laboratory note-book, and are selected so as to show the difference in behaviour between a very soluble salt such as CsCl and a less soluble one. Each is typical of its class:—

Time.	Corrected barometer.	Level of solution above orifice.	Rate of steam condensed and measured in E.	Corrected balance-point on bridge.	Mean.	Temperature difference from hypsometer.	Remarks.
Experiment with Na_2SO_4 on March 10, 1910. Bridge Extension [2] used (*Cf.* preceding paper, p. 478).							
A.M.		cm.				°C.	
9.30							Lit up.
10.25	743·7	7·0		132·70			
10.35			20·8 c.c. in 10′	132·96			
10.45				133·03			
11.0	744·3	7·25		133·02	133·02	2·9334	
11.15		7·35		133·02			
11.30				133·20			
11.45	744·3	7·5		133·29	133·29	2·9372	
12.0		7·5		133·29			
12.20				133·39			
12.35		7·85		133·41	133·42	2·9391	
12.50	744·3	7·95		133·47			
Experiment with CsCl on October 9, 1910. Bridge Extensions [2] and [16] used.							
9.30							Lit up.
10.5	751·3						
10.20		2·5	30·0 c.c. in 10′	91·5			
10.30	751·2	2·75		93·73			
10.35	751·2	2·9		95·09	95·09	19·879*	
10.45	Found all the salt dissolved and the temperature falling rapidly; added more salt						
11.0	751·2	3·7		95·60			
11.5				95·56			Temp. falling, added salt.
11.25	751·2	4·8		96·12			
11.30		4·9		96·53			
11.35	751·2	5·1		97·27	97·26	19·912*	Added salt.
11.40		5·1		97·25			
11.55	751·1	6·4	30·0 c.c. in 10′	98·24			
12.0		6·55		98·79			
12.5		6·7		98·89	98·91	19·936*	
12.10	751·0	6·8		99·06			
12.25		7·2		100·13	100·26	19·957*	
12.35	751·0	7·4		100·39			

It should be mentioned that the numbers given under the heading "corrected balance-point on bridge" are the null points calculated from the observed deflections when the contact was 1 mm. above and 1 mm. below the null point, both readings being repeated with the current reversed. This value is then corrected for errors in the bridge wire and for slight inequalities in the proportional arms.

The numbers marked with an * are derived from the "means" by correcting the latter to a constant barometer pressure of 750 mm., by the aid of a "barometer coefficient" = 0·00608° C. = 0·42 bridge mm. per millimetre of mercury. This barometer coefficient is discussed below.

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The Barometer Coefficients.—The effect of changes in barometric pressure on the temperature equilibrium is greater in the case of saturated solutions than with water. This is in part due to changes of solubility with pressure, and results, to a certain degree, in making the differential arrangement of the platinum thermometers not so effective in eliminating the variations in barometric height.

We have therefore arranged the observations (by determining boiling points at differing barometric pressures) so that a barometer coefficient may be calculated for each salt; in every case the coefficient is derived from the mean of two or more determinations, and it represents the excess of the effect on the temperature of the boiling saturated solution produced by a rise of barometer of 1 mm. over the corresponding effect on the temperature of the steam in the hypsometer.

The magnitude of the coefficient depends upon the solubility of the salt and also on the temperature coefficient of solubility; thus for Na_2SO_4, which is only moderately soluble and does not vary in solubility with temperature, the coefficient is only 0·00052° C., while for KNO_3, which has both a high solubility and a large temperature coefficient of solubility, the coefficient is 0·0217° C.

The barometer readings given in the tables were obtained thus:—Before an experiment, the standard barometer (it was standardised at Kew) was compared with a Callendar sulphuric acid barometer of a large size; the latter had been adjusted successfully so as to have practically no temperature coefficient (its sensitiveness was such that 1 mm. change in the mercury barometer caused a change in it of 2·05 mm.), and all readings during the experiment were taken on the Callendar instrument.

Results of the Observations.—The following tables give the results of the observations. It was found that variations in the rate of passage of steam make but little difference to the extrapolated (see later) "equilibrium" temperature for zero height of liquid, so that these rates are not tabulated but two sets of observations are given for TlCl and for Cs_2SO_4 to show the effect. The last column of figures in each table gives the rise in temperature above the hypsometer for a constant barometric pressure which is somewhere near the mean of the various pressures noted in the second column; these numbers are calculated by means of the barometer coefficient given at the head of the table:—

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Table I.

Height above orifice.	Corrected barometer.	Observed rise in temperature above hypsometer.	Corrected rise.
NaCl. (Bar. coeff. = 0·00103° per mm. Hg.)			
cm.	mm.	° C.	° C.
2·35	745·4	8·6809	8·6805 Corrected to 745 mm. Hg.
3·47	744·0	·6942	·6952 ,, ,,
3·8	733·4	·6894	·7013 ,, ,,
4·3	741·0	·7069	·7110 ,, ,,
[4·8	723·9	·7077	·7294]* ,, ,,
4·85	729·0	·7021	·7186 ,, ,,
5·0	744·4	·7189	·7195 ,, ,,
7·0	751·1	·7573	·7510 ,, ,,
* A single unconfirmed determination.			
KCl. (Bar. coeff. = 0·00242° per mm. Hg.)			
3·55	746·5	8·5868	8·5953 Corrected to 750 mm. Hg.
4·55	744·6	·5915	·6046 ,, ,,
5·05	758·8	·6350	·6137 ,, ,,
5·15	756·5	·6231	·6067 ,, ,,
5·5	746·9	·6011	·6086 ,, ,,
5·5	748·6	·6039	·6073 ,, ,,
8·45	744·4	·6340	·6476 ,, ,,
RbCl. (Bar. coeff. = 0·0021° per mm. Hg.)			
1904 salt—			
3·07	750·6	13·7090	13·7078 Corrected to 750 mm. Hg.
4·1	750·2	·7200	·7196 ,, ,,
4·85	752·3	·7332	·7284 ,, ,,
5·4	750·2	·7424	·7420 ,, ,,
7·05	751·7	·7707	·7671 ,, ,,
Impure—			
2·8	747·4	·7304	·7359 ,, ,,
4·0	747·8	·7514	·7560 ,, ,,
4·8	750·0	·7603	·7603 ,, ,,
5·6	749·3	·7688	·7705 ,, ,,
1st recrystallisation—			
2·55	747·9	·7086	·7130 ,, ,,
3·5	746·9	·7228	·7293 ,, ,,
2nd recrystallisation—			
2·4	753·2	·7135	·7068 ,, ,,
4·35	747·1	·7202	·7263 ,, ,,
5·8	747·6	·7430	·7480 ,, ,,
CaCl. (Bar. coeff. = 0·00608° per mm. Hg.)			
2·4	750·8	19·8842	19·8793 Corrected to 750 mm. Hg.
3·2	750·8	·8917	·8868 ,, ,,
3·6	744·6	·8613	·8941 ,, ,,
4·6	750·8	·9162	·9113 ,, ,,
6·2	750·6	·9405	·9369 ,, ,,
6·9	750·6	·9606	·9570 ,, ,,

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Table I—*continued.*

Height above orifice.	Corrected barometer.	Observed rise in temperature above hypsometer.	Corrected rise.	
		TlCl. (Bar. coeff. = 0·00029° per mm. Hg.)		
cm.	mm.	° C.	° C.	
2·9	751·3	0·0996	0·1000	Corrected to 750 mm. Hg.
3·0	735·7	·0964	·1005	„ „
3·0	752·5	·1004	·0997	„ „
3·15	748·5	·1004	·1008	„ „
3·3	737·4	·0971	·1008	„ „
3·55	742·2	·0996	·1019	„ „
3·8	750·5	·1054	·1053	„ „
3·8	743·3	·1030	·1049	„ „
4·0	746·3	·1040	·1051	„ „
4·8	748·0	·1077	·1083	„ „
4·95	757·0	·1125	·1105	„ „
5·1	749·5	·1117	·1118	„ „
5·5	748·0	·1146	·1152	„ „
7·0	748·4	·1310	·1315	„ „
		Another set with a higher rate of steam.		
2·4	728·9	0·0971	0·0974	Corrected to 730 mm. Hg.
2·9	729·4	·1005	·1007	„ „
3·4	730·0	·1043	·1043	„ „
4·3	730·4	·1084	·1083	„ „
5·2	734·1	·1136	·1124	„ „
5·25	732·2	·1136	·1130	„ „
7·0	727·2	·1284	·1292	„ „
7·1	731·9	·1295	·1289	„ „
		Na_2SO_4. (Bar. coeff. = 0·00052° per mm. Hg.)		
3·77	742·2	2·9031	2·9046	Corrected to 745 mm. Hg.
4·15	749·45	·9100	·9077	„ „
4·35	749·45	·9124	·9101	„ „
4·95	744·4	·9164	·9167	„ „
5·1	743·95	·9185	·9190	„ „
5·7	740·35	·9203	·9227	„ „
5·75	742·4	·9228	·9242	„ „
6·75	743·85	·9335	·9341	„ „
7·0	743·85	·9374	·9380	„ „
7·3	742·7	·9418	·9430	„ „
		K_2SO_4. (Bar. coeff. = 0·00014° per mm. Hg.)		
2·3	763·2	1·3967	1·3963	Corrected to 760 mm. Hg.
3·6	763·6	·4027	·4022	„ „
4·05	750·1	·4044	·4058	„ „
4·3	750·1	·4063	·4077	„ „
5·8	762·9	·4210	·4206	„ „
6·85	763·2	·4365	·4361	„ „
		Rb_2SO_4. (Bar coeff. = 0·00043° per mm. Hg.)		
4·5	746·3	3·5373	3·5389	Corrected to 750 mm. Hg.
4·5	754·0	·5395	·5378	„ „
5·45	745·8	·5465	·5483	„ „
5·6	745·8	·5491	·5509	„ „
5·95	754·0	·5577	·5560	„ „
6·2	754·0	·5621	·5604	„ „
7·1	755·0	·5751	·5730	„ „

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Table I—*continued.*

Height above orifice.	Corrected barometer.	Observed rise in temperature above hypsometer.	Corrected rise.	
	Cs_2SO_4. (Bar. coeff. = 0·00100° per mm. Hg.)			
cm.	mm.	° C.	° C.	
2·55	750·4	9·9701	9·9697	Corrected to 750 mm. Hg.
3·2	750·4	·9774	·9770	,, ,,
4·58	747·5	·9852	·9877	,, ,,
4·95	755·7	10·0063	10·0006	,, ,,
5·1	747·6	9·9954	9·9978	,, ,,
5·3	747·5	10·0024	10·0049	,, ,,
6·2	747·5	·0244	·0269	,, ,,
6·25	755·5	·0304	·0249	,, ,,
	Another set with a higher rate of steam.			
2·2	749·4	9·9714	9·9720	Corrected to 750 mm. Hg.
2·7	744·5	·9729	·9784	,, ,,
3·62	745·3	·9852	·9899	,, ,,
3·65	751·3	·9899	·9886	,, ,,
3·75	756·2	·9974	·9912	,, ,,
4·4	755·7	10·0057	10·0000	,, ,,
5·1	749·9	·0181	·0182	,, ,,
	Tl_2SO_4. (Bar coeff. = 0·00022° per mm. Hg.)			
4·3	746·5	0·3293	0·3301	Corrected to 750 mm. Hg.
4·75	742·9	·3317	·3333	,, ,,
5·1	748·8	·3352	·3355	,, ,,
5·7	739·7	·3367	·3390	,, ,,
5·9	752·1	·3427	·3422	,, ,,
6·1	752·5	·3446	·3440	,, ,,
6·3	752·3	·3472	·3467	,, ,,
	$NaNO_3$. (Bar. coeff. = 0·00835° per mm. Hg.)			
5·6	743·7	20·1102	20·1211	Corrected to 745 mm. Hg.
5·75	738·4	·0671	·1222	,, ,,
6·0	743·8	·0195	·1295	,, ,,
6·95	745·9	·1506	·1431	,, ,,
7·4	751·7	·2001	·1442	,, ,,
8·2	745·8	·1681	·1614	,, ,,
8·4	751·3	·2242	·1716	,, ,,
9·2	739·9	·1452	·1878	,, ,,
	KNO_3. (Bar. coeff. = 0·0217° per mm. Hg.)			
2·5	746·1	15·2950	15·3796	Corrected to 750 mm. Hg.
3·6	747·9	·3614	·4070	,, ,,
3·7	750·5	·4224	·4116	,, ,,
5·4	750·0	·4596	·4596	,, ,,
7·2	746·2	·4161	·4986	,, ,,
9·8	746·3	·4900	·5703	,, ,,
	$CsNO_3$. (Bar. coeff. = 0·0044° per mm. Hg.)			
3·6	753·1	7·2193	7·2057	Corrected to 750 mm. Hg.
4·05	751·5	·2182	·2116	,, ,,
4·2	751·4	·2163	·2111	,, ,,
4·6	751·4	·2312	·2250	,, ,,
5·3	751·4	·2397	·2335	,, ,,
5·7	751·4	·2483	·2421	,, ,,
7·3	751·0	·2974	·2930	,, ,,

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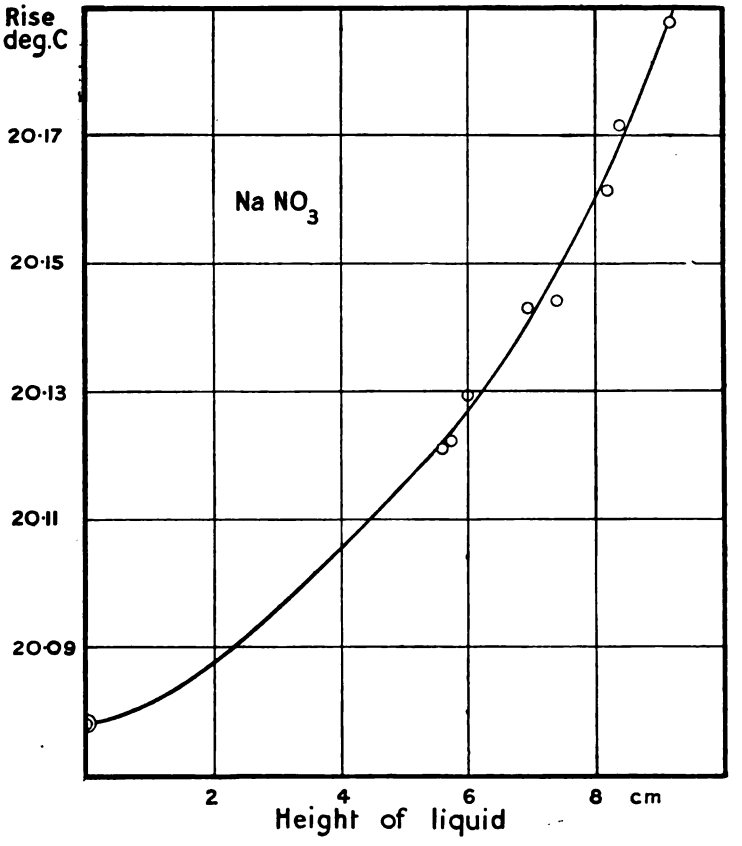
Table I—*continued.*

Height above orifice.	Corrected barometer.	Observed rise in temperature above hypsometer.	Corrected rise.
	$Sr(NO_3)_2$. (Bar. coeff. = 0·00200° per mm. Hg.)		
cm.	mm.	° C.	° C.
3·9	735·7	6·7577	6·7663 Corrected to 740 mm. Hg.
4·05	741·1	·7714	·7692 „ „
5·3	739·6	·7785	·7793 „ „
5·45	735·7	·7737	·7823 „ „
7·45	735·7	·7996	·8062 „ „
	Cæsium alum. (Bar. coeff. = 0·00115° per mm. Hg.)		
2·5	745·8	0·5191	0·5182 Corrected to 745 mm. Hg.
3·7	735·3	·5121	·5232 „ „
3·8	745·8	·5248	·5289 „ „
5·0	745·9	·5347	·5337 „ „
5·1	745·9	·5362	·5352 „ „
6·1	745·9	·5458	·5448 „ „

We give some curves, where the corrected rise is plotted against height, for three salts of widely different solubilities; these may be taken as types for the others.



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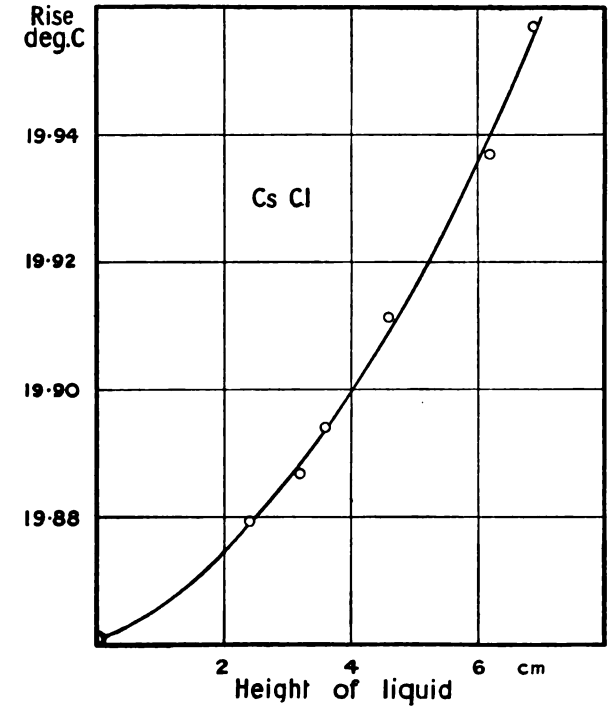

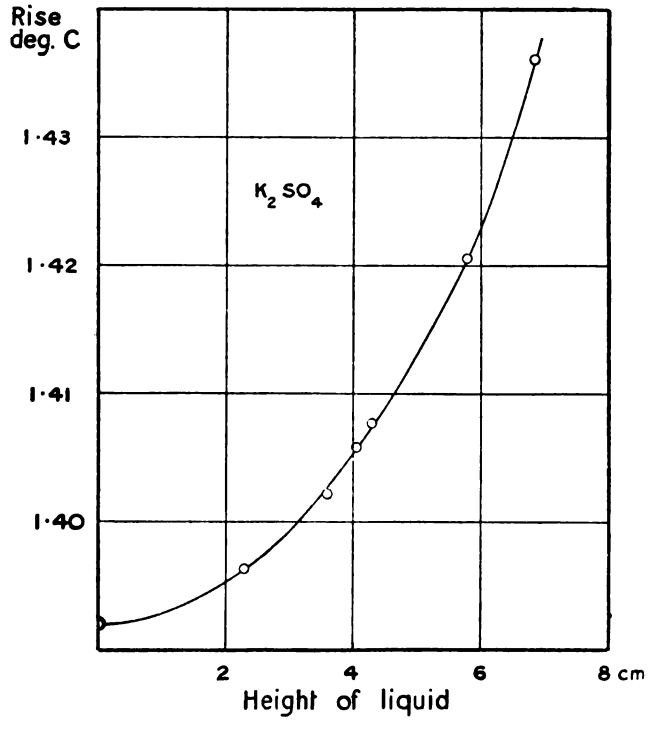

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The following table gives a comparison between Buchanan's* barometer coefficients and ours for the salts we both have worked with:—

Table II.

Salt.	Barometer coefficient.	
	Buchanan's.	B. and A.'s.
	°C.	°C.
NaCl	0·0018	0·00103
KCl	0·0032	0·00242
$NaNO_3$	0·0128*	0·00835
K_2SO_4	0·00087	0·00014

* All Buchanan's observations on $NaNO_3$ were made with the barometer below 620 mm.

Theory.—In the case of water, where the curve connecting the equilibrium temperature with the height of liquid is known to cut the temperature axis at the hypsometer point, we were able to derive an equation, from theoretical considerations, which fitted the observations. This equation shows the curve to be a hyperbola.

In conformity with the definition previously given of the boiling point of a solution, it is required, in the present case, to obtain a means of correctly extrapolating to the equilibrium temperature at zero height of liquid.

On plotting the numbers under the heading "corrected rise" against the height of solution (see typical curves on pp. 496–7), it is at once apparent that, as for water, the graphs are not straight lines, but are convex to the axis along which the depth of solution is measured. The obvious similarity between the water and solution curves suggests that the latter are also hyperbolas.

If, on the one hand, we extrapolate to zero height by means of a bent steel ruler, and on the other we calculate the same point on the assumption that a hyperbola fits the observations, we get the numbers given in Table III.

It is evident that a considerable divergence exists between the two methods of extrapolating; in most cases the difference is greater than the experimental error.

The theoretical formulæ developed in the preceding paper are applicable in their entirety to the saturated solutions—for although the conditions of the experiments here considered differ in some respects from those pertaining to water, they, as will be shown, scarcely affect the argument.

* Buchanan, 'Trans. Roy. Soc. Edin.,' 1899, vol. 39, p. 529.

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The principal differences are detailed in paragraphs (*a*), (*b*), (*c*), and (*d*) below.

(*a*) There is no question but that the liquid is now entirely heated by the condensation of steam; for in most cases the temperature of the entering steam is less than that of the solution, and the latter is only heated because its vapour-pressure is less than the steam pressure.

Table III.

Substance.	Barometer.	Rise by steel ruler.*	Calculated rise.
	mm.	°C.	°C.
NaCl	745	8·640	8·653
KCl	750	8·567	8·576
RbCl	750	13·682	13·689
CsCl	750	19·861	19·861
TlCl	750	0·091	0·094
„	730	0·086	0·090
Na_2SO_4	745	2·880	2·877
K_2SO_4	760	1·387	1·392
Rb_2SO_4	750	3·502	3·506
Cs_2SO_4	750	9·953	9·953
„	750	9·955	9·955
Tl_2SO_4	750	0·312	0·315
$NaNO_3$	745	20·037	20·078
KNO_3	750	15·310	15·332
$CsNO_3$	750	7·163	7·184
$Sr(NO_3)_2$	740	6·742	6·750
Cæsium alum	745	0·506	0·511

* This extrapolation was done separately by two unbiassed observers, and the numbers tabulated are the mean of their results.

(*b*) The possible cooling effect taking place through the walls of the boiling vessel; this, in the case of high boiling points, might at first sight be thought to cause a considerable loss of heat, but when it is remembered that the walls of the outer vessel are thoroughly lagged, it can be safely assumed that most of the heat lost by the solution in this way is returned to it by the extra heat imparted to the entering steam, so that the balance is scarcely disturbed.

(*c*) The rate of increase in the depth of some of the solutions was much faster than in the case of water, in fact it was as much as 3 mm. in 10 minutes (the quantity of steam passing through the solution in the same time was 30 grm.); this phenomenon prevented us from reaching a true equilibrium. The results, however, are unaffected, for the depth of solution was always measured shortly before and after the temperature was determined, and these numbers were used for the curve.

It should be mentioned that a momentary maximum temperature can always be reached, but this maximum is not the true boiling point of the

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saturated solution; it can be realised easily that the maximum only shows when the quantity of salt left in the liquid is not enough to keep it saturated; this, indeed, was quite apparent to the eye. No temperatures here recorded are other than those that we are satisfied belong to solutions which were saturated at the time of observation.

(*d*) The mean area of a bubble may still be taken as constant; for even supposing that the whole change of level in the solution were caused by steam condensed out of the bubbles as they rise, the consequent change in area will only be small. Thus, taking the most rapid rise of all (cæsium chloride), where the level changed by a height equivalent to 3 c.c. in 10 minutes, while the amount of steam condensed in the condenser was 30 grm., the consequent volume change in the bubbles is only about 9 per cent., and the area change 5 per cent. This quantity may be neglected in view of the fact that the rise of level is largely caused by steam condensing (and running back into the solution) on the exposed walls of the boiling vessel, which may be taken to be covered by a relatively cold film of solution thrown there by the breaking bubbles. That this explanation is correct is shown by the fact that, with all the salts, the depth of liquid had no appreciable influence on the rate at which the level rose; in other words, the rise is approximately independent of the number of steam bubbles in contact with the liquid.

Final Results for the Boiling Points.—In view of the previous discussion, it may be assumed that the curve of boiling point plotted against height of liquid is a hyperbola.

On this assumption we have extrapolated to a height $h = 0$, by two methods, one by calculation from equation (2) of the previous paper, and the other by a very convenient method suggested to us by Mr. A. F. Pedder, of Magdalen College (Oxford).—See Appendix II.

For the first method we passed a smooth curve through the experimental points, and using this curve to obtain the constants of the equation, we deduced a value for t when $dt/dh = 0$; in the second method, which is applicable to any hyperbola (not necessarily one which cuts the axis of temperatures at right angles), we extrapolated from the actual experimental points to the point where the curve cuts the temperature axis.

The greatest divergence between the results of the two methods was 0·016° C. for sodium nitrate, where the experiments, owing to the high solubility, were somewhat inaccurate. Except for this discrepancy, the deviation was never greater than 0·01°, and was usually much less.

We would lay considerable emphasis on this fact; for it seems to be confirmatory evidence for the validity of the various assumptions that we

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have made during the theoretical discussion both in this communication and in that on the boiling point of water.

The means of the two methods of extrapolating are given in the following table and are the final results for $h = 0$. The second column gives the

Table IV.

Substance.	Barometer.	Boiling point under pressure in second column.	Boiling point under standard conditions.	Buchanan's boiling points extrapolated to 760 mm.
	mm.	° C.	° C.	° C.
NaCl	745	108·096	108·668	108·50
KCl	750	108·205	108·599	108·35
RbCl	750	113·318	113·710	
CsCl	750	119·488	119·919	
TlCl	750	99·724	100·097 (100·098)	
"	730	98·967	100·099	
Na_2SO_4	745	102·320	102·885	
K_2SO_4	760		101·392	101·41
Rb_2SO_4	750	103·136	103·511	
Cs_2SO_4	750	109·583	109·963 (109·964)	
"	750	109·585	109·965	
Tl_2SO_4	750	99·945	100·317	
$NaNO_3$	745	119·514	120·20	118·71
KNO_3	750	114·962	115·549	
$CsNO_3$	750	106·814	107·228	
$Sr(NO_3)_2$	740	106·005	106·790	106·52
Cæsium alum ...	745	99·954	100·527	

height of the barometer to which the boiling points given in the third column have been corrected, while the fourth column gives the boiling points corrected to 760 mm. pressure and to sea level and latitude 45°. The fifth column gives Buchanan's values extrapolated to a barometer pressure of 760 mm.

Experimental Error.—In view of the close agreement shown to obtain in the two methods of extrapolation, and also in the two sets of observations for TlCl and Cs_2SO_4 we think we may say that the final boiling points probably do not differ from the truth by more than 0·005° C.; this involves all errors in the barometer coefficients, but the actually observed boiling points for the same height and rate of bubbling agree more closely.

The Osmotic Pressures.—One of us pointed out in a letter to 'Nature'* that osmotic pressures derived from vapour-pressure observations can be measured in two ways—one, with the pressure on the solvent constant, and the other with the constant pressure on the solution; in the former case, as can be seen from Prof. Porter's fundamental equation,† it is necessary to determine the space occupied by the solvent in the solution, and this involves a series of

* 'Nature,' 1906, vol. 74, p. 7.

† 'Roy. Soc. Proc.,' A, 1907, vol. 79, p. 521.

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measurements of the compressibilities together with the densities of the solutions.

Prof. Porter's fundamental equation, for the case where the pressure on the solution is its own vapour pressure, becomes*

$$\int_{\pi_\pi - P_\pi}^{\pi_\infty} u dp = \int_{\pi_\pi}^{\pi_\infty} v dp, \qquad (1)$$

where π_{00} is the vapour-pressure of the solvent when under the hydrostatic pressure of its own vapour, π_π is the vapour-pressure of the solution, v is the specific volume of the vapour, u is the specific volume of the pure solvent, p is the hydrostatic pressure, and P_π is the osmotic pressure when the solution is under the hydrostatic pressure of its own vapour. This equation, neglecting the pressure effect of the slightly different vapour-pressures of different solutions, enables us to bring the calculated osmotic pressures of solutions of different solutes (in the same solvent) into direct comparison. It, however, involves (as the u term shows) a knowledge of the specific volume and compressibility of the pure solvent when under a negative pressure.

Equation (1) reduces to

$$P = \pi_{00} v \log_e \pi_{00}/\bar{u} - \pi_{00} + \pi_\pi,$$

where $\bar{u}$ is the mean value of the specific volume of water between the limits in the integral; this value, in the calculations, has been obtained by extrapolating to negative pressures the known compressibility of water.

The results of the calculations are given in the following table:—

Table V.

Salt.	Boiling point.	$\bar{u}$.	Osmotic pressure.	No. of grm. mols. per litre of solution.	Osmotic pressure / Grm. mols. per litre
			atmos.		
NaCl	108·668	1·0628	476·8	5·648	84·4
KCl	108·599	1·0627	473·3	5·985	79·1
RbCl	113·510	1·0742	743·2	7·948	93·5
CsCl	119·919	1·0883	1055·0	9·214	114·5
TlCl	100·097	1·0443	5·5	0·097	57·0
Na_2SO_4	102·885	1·0498	162·2	2·596	62·5
K_2SO_4	101·392	1·0465	79·4	1·255	63·2
Rb_2SO_4	103·511	1·0513	197·0	2·505	78·6
Cs_2SO_4	109·963	1·0658	545·4	4·015	135·8
Tl_2SO_4	100·317	1·0443	17·8	0·347	51·3
$NaNO_3$	120·20	1·0888	1062·9	12·276	86·6
KNO_3	115·549	1·0786	838·3	12·756	65·7
$(RbNO_3$	119·4	1·0875	1041·0	12·828	81·2)
$CsNO_3$	107·228	1·0596	398·1	6·617	60·2
$(TlNO_3$	104·7	1·0541	264·0	11·058	23·9)
$Sr(NO_3)_2$	106·790	1·0587	376·2	3·588	104·8
Cæsium alum	100·527	1·0443	21·2	0·300	70·1

* Porter, *loc. cit.*, p. 523.

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The values for the numbers within the brackets are obtained from an earlier communication to the Society,* but the boiling points are not very accurate; we have not yet been able to get satisfactory results with these salts.

It is noticeable that the numbers in the last column for alkali salts which have the same anion seem to increase with increasing molar concentration.

On comparing the numbers in the fourth and fifth columns it will be seen that all the salts, except $TlNO_3$, are dissociated. As already mentioned, the results for $TlNO_3$ are not reliable, but in view of the importance of such an exception we are making further experiments to decide the question.

Appendix I.

Solubilities and Densities of Saturated Solutions of Strontium Nitrate.—The densities and solubilities of all the salts dealt with in this communication, except strontium nitrate, were recorded together with the method of work in a previous paper; the following results for the strontium salt were obtained in the manner therein detailed:—

Table VI.

Temperature.	Density.	Weight concentration (number of grammes of anhydrous salt in 100 grammes of water).
°C.		grammes.
0·58	1·28561	40·124
14·71	1·39380	60·867
26·40	1·48831	82·052
29·06	1·51098	87·648
30·28	1·51441	88·577
32·58	1·51408	88·943
39·74	1·51282	90·086
47·73	1·51150	91·446
61·34	1·51048	93·856
68·96	1·51057	95·576
78·98	1·51091	97·865
88·94	1·51174	100·136

These densities and solubilities were plotted against the temperature, and were found to give a transition point of 29·5° C. and 29·4° C. respectively. Mulder (from Landolt and Börnstein) obtained 31·3° and Etard† 32° C. for this point. The discrepancy is so large that it was thought advisable to make some further observations; the results are given below.

A cooling curve of the saturated solution of a sample which had been used

* 'Phil. Trans.,' A, 1904, vol. 203.

† 'Annales,' [7], vol. 2, p. 528.

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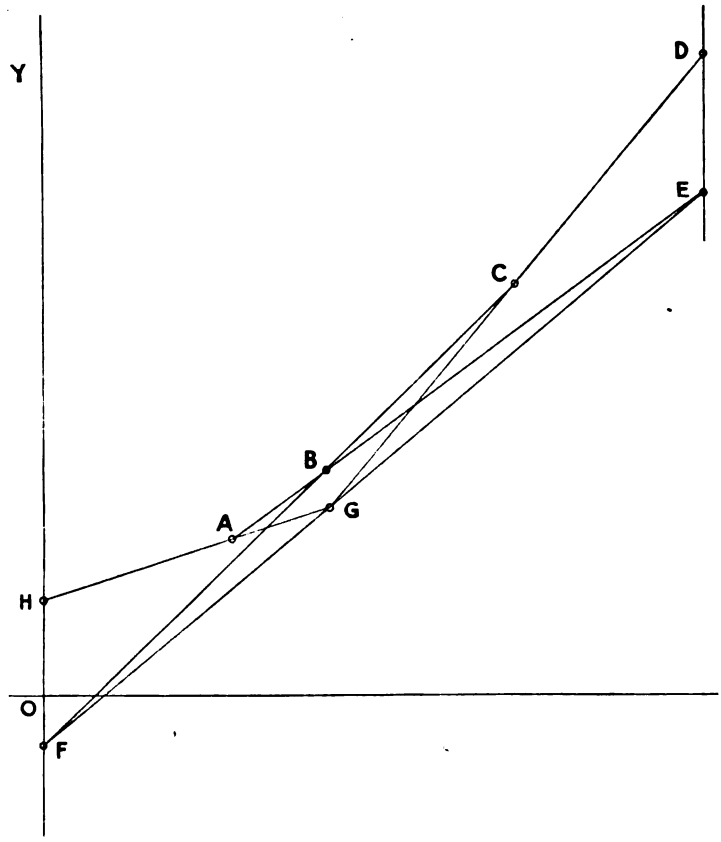
for the boiling points gave the transition point as 29·3°, when the super-cooling had been 1·4°. Another similar sample after recrystallisation also gave 29·3° (super-cooling 1°).

An experiment made with a dilatometer, using turpentine as index liquid, gave the transition point as 29·22°.

Appendix II.

Given four points A, B, C, and D, on a hyperbola which has an asymptote parallel to the axis OY of reference (see the diagram); required to find the point of intersection between the hyperbola and OY. The points A, B, C, D, and a point I, on the asymptote at infinity, may be regarded as five of the angular points of a hexagon inscribed in the hyperbola; a sixth point is on OY.



By a well-known theorem the points of intersection of the three pairs of opposite sides of a hexagon inscribed in a conic lie on a straight line.

Join AB and produce it to cut ID produced (the ordinate through D) at

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E; join BC and produce it to cut the side OY at F; join EF. Join DC and produce it to cut EF in G; join GA and produce it to cut OY in H. It is easy to see that H is the point required.

Pendulum Clocks and their Errors.

By H. R. A. Mallock, F.R.S.

(Received May 27,—Read June 29, 1911.)

The measurement of time by pendulum clocks is one of the most accurate measures in daily use, but even with the best existing clocks it is not uncommon to find that the rate may vary from time to time by as much as half a second a day, roughly about 1 part in 150,000.

Clocks are rated by comparison with the rotation of the earth, which is assumed to be constant, and it is a matter of some interest to inquire into the possibility of making a clock good enough to rate the earth by.

The gradual reduction of the angular velocity of the earth as deduced from astronomical data used to be taken as about 22 seconds per century,* but I believe that this estimate is now considered too high.†

At any rate, if a clock is to be accurate enough to give a measure of the change in the earth's angular velocity, it must have a variation of rate not much exceeding one second per century, or about 1 part in 3,000,000,000. It seems hardly possible that this order of accuracy should be reached by any mechanical appliance.

In the following notes, however, I have stated the various causes which may bring about a change in the rate of a pendulum, and the permissible variation of the different arguments involved if the variation of rate due to each of them is not to exceed 1 part in 100,000,000.

The causes of variation of rate may be grouped under three heads, namely:—

(*a*) Such as would affect a pendulum swinging freely *in vacuo*.

(*b*) Variations due to the action of the atmosphere on a free pendulum.

(*c*) Variations due to the action of the mechanism which maintains the vibration.

Of these it will be seen that (*c*) is the most important and the most

* Thomson and Tait, vol. 1, Part I, p. 400.

† Variation of the length of the day due to contraction by secular cooling would not be indicated by a pendulum clock.

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difficult to deal with. In the early days of clock making, before the approximate isochronism of pendulums was properly appreciated, more attention was given to the mechanism than to the escapement, the latter being looked on merely as a sort of brake to prevent the weights running down too fast, but for the last 150 years at least it has been recognised that the function of the clock mechanism was, in the first place, to maintain the swing of the pendulum with as little interference as possible, and, secondly, to count the swings.

In what follows the variations of rate are expressed in fractions of the natural period of the pendulum, and the integral error in the recorded time over any stated period is the same fraction of that period, and is independent of the actual length or natural period of the pendulum.

Beginning with the free, simple pendulum oscillating *in vacuo* with vanishing amplitude; if we take a simple pendulum of length λ, for which $\tau = 2\pi\sqrt{\lambda/g}$ for infinitesimal arcs, then

$$(1)\quad d\tau/d\lambda = \tau/2\lambda, \qquad \text{also} \qquad (2)\quad d\tau/dg = \tau/2g.$$

If we take a pendulum with a bob whose moment of inertia is $M\kappa^2$, $\tau = 2\pi\sqrt{(h^2+\kappa^2)/gh}$ (where h is the length of the pendulum rod measured from the support to the centre of inertia), we have $d\tau/d\kappa = 2\pi\kappa/h\sqrt{gh}$ or $\tau\kappa/h^2$.

(4) A pendulum is only approximately isochronous, and in this respect is at a disadvantage compared with a balance wheel stabilised by a spring.

Keeping only the first terms of the series, expressing the period τ_α in an arc whose circular measure is α, in terms of α and τ_0 (the period for infinitely small arcs), if α is small, $\tau_\alpha = \tau_0(1+\alpha^2/16)$ and $d\tau/d\alpha = \alpha/8$.

(5) Pendulums are generally suspended by a very thin spring, but knife-edges have also been used, and in estimating the equivalent length (λ) corrections are required in both cases.

First as regards spring suspension. The spring is clamped at the upper end and clamped also to the pendulum rod. It can be shown that the equation to the curve into which the spring is bent is (for small pendulum arcs) $y = y_1 e^{-x/p}$. In this equation x is measured along the virtual line of suspension of the pendulum, the axis of Y being the normal to X passing through the point of suspension (see fig. 1), and $p = \sqrt{A/W}$, where W is the weight of the pendulum and A depends on the elastic constant of the spring and its form. For a strip of width b and thickness $2c$, $A = 2nbc^3$ (n being Young's modulus for the material).

The virtual length of the pendulum is shortened by $\sqrt{A/W}$.

(6) If the suspension is by a knife-edge the correction is of a different

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kind. A knife-edge must be regarded as a part of a cylinder of small radius (r) which rolls on the supporting surface. If the pendulum oscillated on the knife-edge as a pivot (*i.e.* if it turned without rolling) the length of the pendulum measured from the axis to the centre of oscillation would be the length of the equivalent simple pendulum. If, as is or always should be the case, the knife-edge rolls on its support, λ is shorter by r than the measured length.

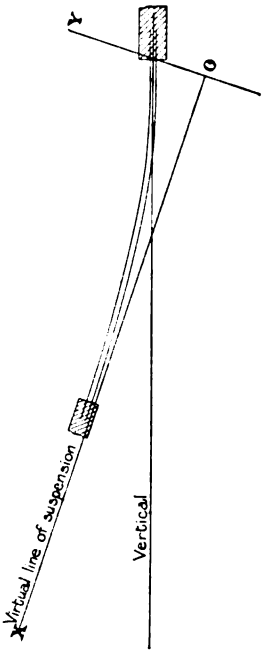

FIG. 1.

It is rather a nice question to determine the best value for r. The smallest value which it can have is determined by the strength and hardness of the material, and if the edge is made too sharp to begin with it will be crushed or deformed in use until either the bearing surface is sufficient to take the stress or (if the support is softer than the knife-edge) it has to some extent embedded itself. In the latter case an angular motion about the axis would involve a certain amount of sliding.

It is not at all an easy matter to work a knife-edge to a truly cylindrical form, and the difficulty increases as the radius diminishes. A very common feature in knife-edges is that of having a small almost flat surface along what would naturally be considered as the edge, and, in fact, it is difficult to handle or place two very hard surfaces in contact without leaving some trace of impact on either.

(7) Suppose that the edge is flattened for a distance a' on each side of the centre line, and that $a' = r\alpha'$, then if $\lambda\alpha$ is the linear amplitude of the vibration of the pendulum, its period will be $\tau_\alpha\left(1-\frac{2}{\pi}\sin^{-1}\frac{r\alpha'}{\lambda\alpha}\right)$, as may be seen from fig. 2. Thus the period diminishes indefinitely with the arc. The motion changes its character when $\lambda\alpha < r\alpha'$.

(8) Another cause which will make the actual period of a given pendulum differ from τ_α is the yielding of supports.

The lateral force exerted by the pendulum on its supports must cause some yielding, and the effect of this on the period of the pendulum may be very simply stated as that of an addition to λ of the length of a pendulum whose period is the natural period of the support when loaded with a mass equal to that of the pendulum.

(9) The length of a pendulum varies during the swing in virtue of the

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stretching of the rod by centrifugal force. The maximum extension due to this is $4W\pi^2\lambda a/nsg\tau^2$, where a is the linear amplitude of the oscillation, s the sectional area of the pendulum rod, and n Young's modulus for the material. The alteration of period is that due to lengthening the pendulum by half this quantity.

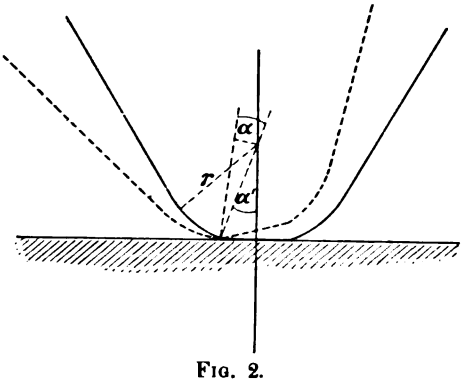

FIG. 2.

(10) In many pendulums mercury is used in the bob for the purpose of compensating temperature effects. The moment of inertia of such a bob differs from that of a solid of the same form, and if the mercury behaved as a perfect fluid the difference would be a function of the shape, and has been calculated for some simple forms.*

When, however, the viscosity of the mercury is taken into account, not only the shape but the absolute period enters into the expression for the moment of inertia in virtue of the rate of propagation of viscous disturbance in the fluid.† In consequence, when the period is very long the liquid bob tends to have the same moment of inertia as a solid of the same form, and when the period is very short the moment of inertia approximates to what it would be if viscosity did not act.

(11) When an oscillation of any kind is opposed by a force proportional to the velocity, and when that force is small compared to the positional force, the alteration of the period of the resisted oscillation is of the second order, but cannot on that account be neglected in the case of pendulums used for the reckoning of time.

The relation between the period τ_a for an unresisted motion of amplitude a, and the actual period τ_a', when resisted, is $\tau_a' = 2\pi\tau_a/\sqrt{(4\pi^2+\beta^2)}$,‡ where

* See Stokes, 'Collected Papers,' vol. 1, p. 188.

† See Lamb's 'Hydrodynamics,' § 328, p. 328.

‡ See Maxwell's 'Electricity,' vol. 2, p. 338, from which this result may be easily deduced.

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β is the angle of the equiangular spiral of which the motion of the resisted oscillation may be taken as the projection. Or, in other words, if $\Delta\alpha$ ($= 2\pi\alpha\beta$) is the diminution of amplitude which occurs in each complete oscillation when the arc is α, then, owing to the extinction, the period is diminished by $\tau_\alpha[1 - 2\pi/\sqrt{(4\pi^2 + \beta^2)}]$, which, when β is small, becomes $\tau_\alpha\beta^2/8\pi^2$.

(12) The effect of a constant resistance on an oscillation is to make each successive arc less than the preceding by a constant quantity. The influence on the period may be gathered from the fact that each time the direction of motion changes sign the zero about which the oscillation takes place is shifted in a direction opposite to that of the motion, and by a constant quantity proportional to the resistance. In fig. 3 let ABC represent the

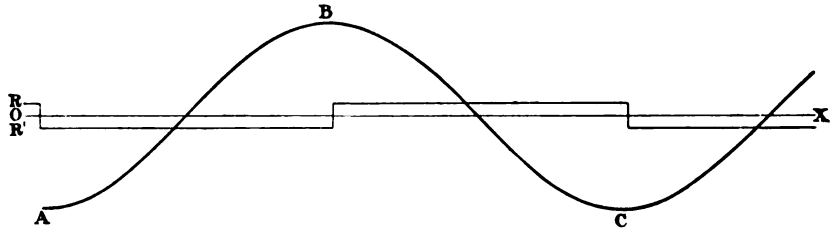

FIG. 3.

unresisted oscillation. Then if OR represent the resistance (on such a scale that the ordinates of ABC represent the positional forces), the retarded oscillation for the half period from A to B will be performed as an unresisted oscillation about the zero axis $y = \mathrm{OR}$, and from B to C as an unresisted oscillation about $y = -\mathrm{OR}$, and the arc α is reduced by OR/λ at each half swing.

Thus, if the time is measured between successive "elongations," the period is unaltered by constant friction; but, between successive crossings of the unresisted zero line, each successive half period is longer than the preceding one by $\frac{\tau}{2\pi}\left(\frac{1}{\alpha_{n+1}} - \frac{1}{\alpha_n}\right)$. When the sum of these excesses reaches the value $\tau/4$, the opposing frictional force is equal to the positional force and the motion ceases.

This proposition is useful in some cases, for it shows that the free period of a pendulum resisted by constant friction can be found, very nearly, by counting the swings until the motion stops, then if the number counted is N, and the whole time is T, the free period is $4\mathrm{T}/(4\mathrm{N}+1)$.

The various causes enumerated above constitute, I believe, a complete list of sources of variation of period which may affect the motion of an unmaintained oscillation *in vacuo* by a quantity exceeding $\tau \times 10^{-8}$.

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If the object of the pendulum observation were to connect λ and g, that is, to deduce a standard of length by gravity experiments, or *vice versâ*, all matters which might affect λ would have to be taken into account, but if the pendulum is merely used as a time-keeper, the variations of λ only, and not the absolute values of h or κ, etc., are of any importance.

Action of the Surrounding Gas.

(13) The air or gas in which the pendulum swings affects the motion in four ways. In the first place, it tends to float the pendulum, and in effect reduces the force of gravity in the ratio of the weight of the displaced air to the weight of the pendulum.

(14) Secondly, assuming for the moment that the air is devoid of viscosity and flows round the pendulum according to the "electric" law, the mass in motion is not only that of the pendulum itself, but it involves also the mass of the disturbed air. This extra mass can be stated as a certain fraction of the mass of a volume of air equal to the volume of the pendulum. The fraction depends on the form of the pendulum (for a cylinder it is unity, and for a sphere $\frac{1}{2}$).

This extra mass, which does not contribute to the positional force, is equivalent to a further reduction of the action of gravity.

(15) Thirdly, when viscosity is taken into account, it is found that, in addition to the mass set in motion by stream-line action, a certain quantity of air is dragged after the pendulum, and that this mass (which also contributes nothing to the positional force) counts as a further reduction in the intensity of gravity.

(16) This, however, is not the only effect which viscosity has, for the motion of the air dragged or rubbed along is not in quite the same phase as the pendulum itself, that is, part of the motion is proportional to the acceleration of the pendulum and part to its velocity.

The latter gives rise to extinction, and alters the period, as mentioned in (11). The investigation of these subjects is due to Stokes.* There is no reason to doubt that the results there given apply to the cases dealt with with sufficient accuracy as far as regards the flotation and stream-line effects, but the treatment of viscosity is more open to question when the velocities concerned are as large as those of clock pendulums. These velocities, indeed, are small in the ordinary sense, but are often sufficient to initiate eddies in the air—an action not taken into account in the calculations.

* 'Collected Papers,' vol. 3, or 'Camb. Phil. Soc. Trans.,' vol. 9.

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Action of the Maintaining Mechanism.

To compensate for the gradual loss of energy which occurs in the oscillations of all real systems, some means must be provided to maintain the motion. This is done by the escapement, which in general consists of an arrangement of wheels and levers driven by a spring or by weights, but whose motion is intermittent, and so controlled by the pendulum itself, that during part of the swing the driving force acts on the pendulum in the direction of its motion.

The mechanical connections between the pendulum and the escapement in most cases give rise to a much greater loss of energy than the free pendulum would suffer from such causes as yielding of its supports and the viscosity of the air. Hence the greater part of the work done by the driving weights goes in making up the loss of which they themselves are the cause.

The desirable qualities in an escapement are that its action should have little effect on the natural period of the pendulum, and, which is more important, that such changes of period as are produced should be as independent as possible of variations of driving force and of the coefficients of friction of the sliding surfaces.

A great number of forms have been given to escapements for pendulum clocks, but the only ones which need be referred to here are the "dead-beat" and the "gravity," since these two have practically superseded all others for accurate time-keeping.

Dead-beat Escapement.

(17) The dead-beat escapement consists of two arcs (fig. 4), AA′ and BB′, of a cylinder whose axis (O) is coincident with the axis of the pendulum. The cylindrical arcs are bounded by the two faces AC, BD, which make the constant angle β with the radius of the cylinder. The radius of the escape wheel and the radius of the cylinder are so taken that OAE and OBE are right angles, and the spacing of the teeth on the escape wheel is such that the distance AB is rather greater than a whole number + one-half times the interval between the successive teeth. Suppose, now, the pendulum to be about to pass through the vertical from right to left; at this moment the tooth on the A side passes from the cylindrical arc A′A and slides over AC, accelerating the motion of the pendulum in the process. After the A tooth has passed, the escape wheel moves round rapidly under the driving force of the clock mechanism, until the B tooth is stopped by the cylindrical arc BB′. Against this arc it rests until the pendulum returns from left to right. The tooth then slides over BD, and again accelerates motion of the pendulum, and so on.

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If μ is the coefficient of friction, and f the force which the tooth of the escape wheel exerts in the direction of its motion, the force normal to the pallet surface is $f/(\mu+\tan\beta)$, and if $OA = OB = r$, the accelerating force on the pendulum bob is $fr/\lambda(\mu+\tan\beta)$, and this force lasts while the pendulum

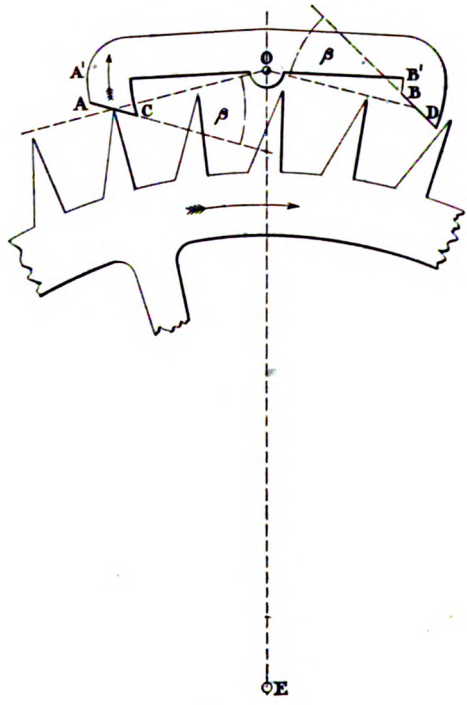

FIG. 4.

oscillates through an angle $\sigma\sin\beta/r$, where σ is the length AC or BD. Except at these times the pendulum is subjected to a retarding force $\mu fr/\lambda$, from the friction of the tooth on the cylindrical arcs AA′ or BB′.

The effect of the escapement forces on the pendulum can be represented graphically.

In fig. 5 let time be measured along OX, and let ABC represent the oscillation of the pendulum ($y = a\sin 2\pi t/\tau$ approximately, where a is the maintained amplitude). Let $y = \pm$ OG and $y = \pm$ OH be straight lines parallel to OX distant κ and e respectively from OX, where $\kappa = fr/\lambda(\mu+\tan\beta)$ and $e = \mu fr/\lambda$. If the scale on which ABC is drawn is such that ordinates represent the gravitational force of restitution as well as the displacement, these lines, as will be readily seen, are the equilibrium positions of the pendulum when acted on by the constant horizontal forces $fr/\lambda(\mu+\tan\beta)$ and $\mu fr/\lambda$, and the oscillation, during the

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intervals for which each force lasts, is in reality a harmonic vibration of period τ_a, but whose virtual amplitude and phase change abruptly with the alteration of the zero position. Thus at P_1 the force changes suddenly

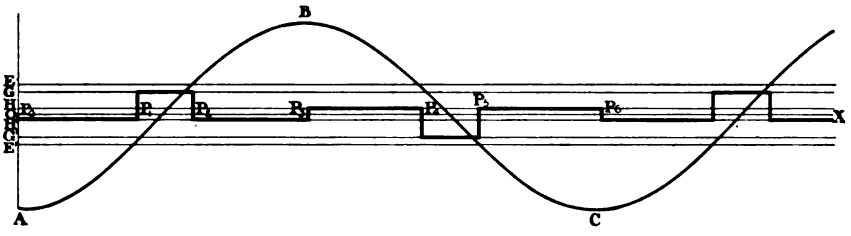

FIG. 5.

from $y - e$ to $y + \kappa$, at P_2 from $y + \kappa$ to $y + e$, at P_3 from $y + e$ to $y - e$ (on account of the change in direction of the motion), and so on. These changes are indicated by the thickened line.

Of course there is no sudden change either in the velocity or position of the pendulum when the zero positions change, and these two conditions, together with the constancy of the period τ_a for all the portions comprised between P_1P_2, P_2P_3, etc., of the oscillation, suggest a simple construction for evaluating the effect of the applied forces on the time which elapses between the successive "elongations," that is on the effective period of the pendulum.

In fig. 6 let

$$\left.\begin{matrix}OE\\OE'\end{matrix}\right\} = \pm h, \qquad \left.\begin{matrix}OG\\OG'\end{matrix}\right\} = \pm \kappa, \qquad \left.\begin{matrix}OH\\OH'\end{matrix}\right\} = \pm e,$$

κ and e having the same meanings as in fig. 5.

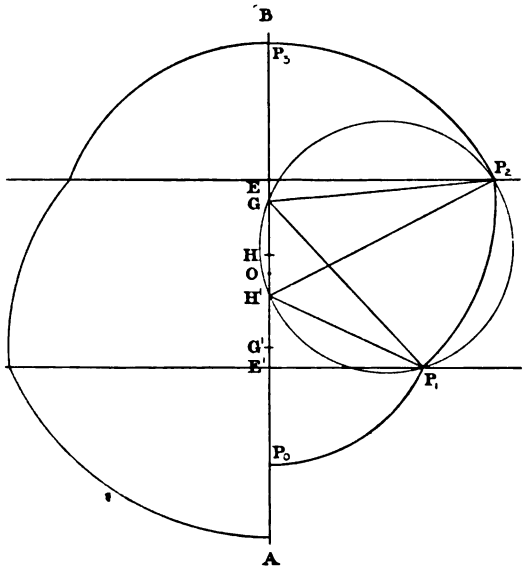

FIG. 6.

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We may imagine the actual motion of the pendulum to be represented by the projection on straight line through AA′ of a point P moving with the constant angular velocity $2\pi/\tau_a$ about the centres H′, G, H′, H, G′, H, in succession. Starting from P_0 the projected motion is resisted by the constant friction e from P_0 to P_1, therefore the point moves in a circle of radius $H'P_0$ about H′; arrived at P_1, the projected motion is accelerated by the force κ due to the action of the tooth of the escape wheel on the pallets, and the point moves in a circle about G from P_1 to P_2; from P_2 to P_3 the motion is again retarded by a force e, and takes place about H′. It is unnecessary to follow the path in detail through P_4, P_5, and P_6.

Let $$P_0HP_1 = \phi_1, \quad P_1GP_2 = \phi_2, \quad P_2H'P_3 = \phi_3;$$

also let $$P_1H'P_2 = \phi'_2.$$

The construction shows that $\phi_1 + \phi'_2 + \phi_3 = \pi$, and if ϕ_2 were equal to ϕ'_2 we should have $\phi_1 + \phi_2 + \phi_3 = \pi$, so that the time taken in describing these three arcs with the angular velocity $2\pi/\tau$ would be $\tau/2$. In this case the applied forces would have made no difference in the period of the pendulum.

The equality between ϕ_2 and ϕ'_2 does not really exist except for certain values of κ and e, although the difference is of the second order.

Draw a circle circumscribing P_1, G, P_2. This circle will, in general, pass close to H′ (if it passes through H′, $\phi_2 = \phi'_2$).

It can be shown that $\phi_2 - \phi'_2$ is nearly equal to the distance (z) (perpendicular to AB) of H′ from the circumscribing circle $\times \sin\phi_1/H'P_2 \sin\phi_2$ (or $\times \sin\phi_2/HP_1 \sin\phi_1$).

In all real cases $\sin\phi_1$, $\sin\phi_2$, $H'P_2$ and HP_1, are so nearly the same that $\phi_2 - \phi'_2$ may be taken as $= z/a$, and the difference in the time of oscillation due to the action of the maintaining and frictional forces is $\tau z/2\pi a$.

As regards the alteration of phase in the different parts of the path; there is a retardation equal to GP_1H' at P_1, and a nearly equal acceleration GP_2H', at P_2. No change of phase occurs at P_0 or P_3.

Supposing that the only dissipative force acting is due to the escapement friction, and that $H'P_1 = a_1$, $GP_1 = a_2$, and $H'P_2 = a_3$, we have $a_2 = a_1 + (\kappa + e)\cos\phi_1$, and $a_3 = a_2 + (\kappa + e)\cos(\phi_1 + \phi_2)$. Now since in real cases both κ and e are so small compared to a that $\frac{1}{2}(\pi - \phi_2) = \phi_1$ and $\frac{1}{2}(\pi + \phi_2) = \phi_1 + \phi_2$, we have $\cos(\phi_1 + \phi_2) = \cos\phi_1$ nearly, so that $a_3 = a_1 + 2(\kappa + e)\cos\phi_1$. If the original amplitude at P_0 measured from O is a_0, $a_0 = a_1 + e$, and the amplitude at P_3 is $a_3 - e$.

Hence, when the escapement has been in action long enough for the motion

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to have become steady, that is, as soon as the frictional loss is just balanced by work done in maintaining the vibration $a_0 = a_3 - e$; therefore

$$\cos \phi_1 = e/(k+e).$$

If the natural loss of amplitude apart from escapement friction is e', we have

$$a_3 = a_1 + 2(\kappa+e)\cos\phi_1 + e' \quad \text{and} \quad \cos\phi_1 = (e+e')/(\kappa+e);$$

and since also $\cos\phi_1 = h/a_0$ nearly,

$$a_0 = h(\kappa+e)/(e+e').$$

This gives the amplitude of the swing in terms of h (the distance on either side of OX (fig. 5) at which the pallets come into action), and of the applied forces other than gravity.

The effect of these forces on the period, when the amplitude remains constant, is very small (of the order less than 10^{-8}), but since the forces represented by κ and e depend on the coefficient of friction between the teeth of the escape wheel and the pallets, a_0 and therefore the period is affected by any change in this coefficient, even if the driving force, f, is constant.

In ordinary clocks, however, in which the escape wheel is driven through a train of wheel work, f itself is subject to variations if, through dirt thickening of oil, or any other cause, the efficiency of the transmission varies.

The investigation just given shows that with a "dead-beat" escapement errors of rate depend on the induced variations of arc of vibration, and not, to any appreciable degree, on the difference of period, which variable friction might be supposed to make in an oscillation of fixed amplitude, and also that the extreme smallness of this direct effect is due to the fact that the maintaining force is applied symmetrically, and lasts for the same time before and after the pendulum passes through the vertical.

Gravity Escapement.

(18) This is made in several forms, but the principle is that the mechanism of the clock alternately raises two small weights, one on either side of the pendulum; these are retained in the raised position until released by the latter some time before it reaches its extreme elongation. The released weight then moves with, and accelerates the motion of, the pendulum until it again passes through the vertical. After this the pendulum is free until it releases the weight on the opposite side, which then moves with the pendulum as did the first, and so on.

While the weights act, the pendulum is virtually oscillating about a zero

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distant $\lambda w/W$ from the vertical; w and W being the weight released by the escapement and the weight of the pendulum respectively.

Figs. 7 and 8 give a diagrammatic picture of the applied forces.

In fig. 7, ABC is the path of the pendulum; the lines through E, E′, F,

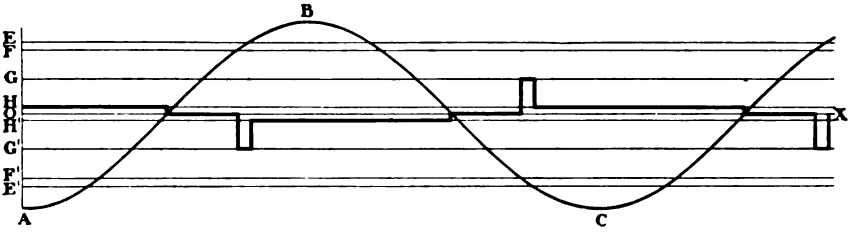

Fig. 7.

and F′ give the distance from the vertical at which the pendulum begins and completes the release of the weights. G and G′ represent the alteration of pendulum zero which occurs while the release is being accomplished, H and H′ in the same way represent the zero alteration due to the action of the weights. The thickened line indicates the sequence in time of the applied forces.

Supposing, as in the case of the "dead-beat," that the motion of the pendulum is represented by the projection of a point moving with uniform angular velocity about the successive zero positions, in fig. 8 (the lettering

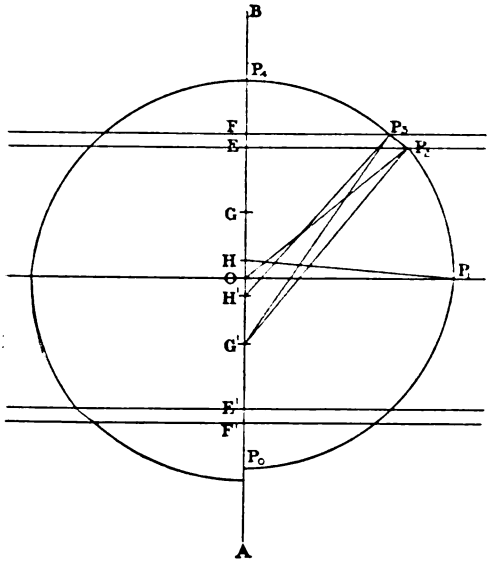

Fig. 8.

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being the same as in fig. 7) let $OE = OE' = h$; $EF = E'F' = \delta h$; $OG = OG' = \kappa$; $OH = OH' = e$. Starting from P_0, let the initial amplitude $OP_0 = a_0$, and let $HP_0 = HP_1 = a_1$, $OP_1 = OP_2 = a_2$, $GP_2 = GP_3 = a_3$ $H'P_2 = P'P_4 = a_4$, and let $OP_4 = a_\pi$, *i.e.* the amplitude after the first half oscillation.

Let $P_0HP_1 = \phi_1$, $P_1OP_2 = \phi_2$, $P_2G'P_3 = \phi_3$, $P_3H'P_4 = \phi_4$.

We have to find a_π and $\phi_1+\phi_2+\phi_3+\phi_4$ in terms of a_0, h, δh, κ, and e; and if we assume, as is true in real cases, that κ and e are small compared to h (and of course to a_1) we have $a_1 = a_0+e$, $a_2 = a_1$, $a_3 = a_1+\kappa h/a$, $a_4 = a_3-(\kappa-e)h/a$, also $\phi_1 = \pi/2-e/a$, $\phi_3 = \delta h/\sqrt{(a^2-h^2)}$, and $P_2OP_3 = \phi_3 a_3/a_4$.

Now $$e/a+\phi_1+\phi_2-P_2OP_3+\phi_4 = \pi,$$

or $$\phi_1+\phi_2-\phi_3 a_3/a_4+\phi_4 = \pi-e/a.$$

Thus $$\phi_1+\phi_2+\phi_3+\phi_4 = \pi-e/a-\phi_3(1-a_3/a_4).$$

From these equations we find, approximately,

$$a_\pi = [a_0^2+e(a_0+h)]/(a_0+e)$$

and $$\pi-(\phi_1+\phi_2+\phi_3+\phi_4) = \frac{e}{a+e}+\delta h\frac{h\kappa}{\sqrt{a^2-h^2}(a^2+eh)}.$$

The gain in amplitude $(a_\pi-a_0)$ therefore is $eh/(a+e)$ and the time of the oscillation is less than τ_a by

$$\frac{\tau}{2\pi}\left(\frac{e}{a+e}+\delta h\frac{h\kappa}{\sqrt{a^2-h^2}(a^2+eh)}\right).$$

The second term in the bracket is the smallest, but it is also the most variable, for it is affected not only by the variation of the coefficient of friction during the release of the weights, but also by any change in the efficiency of the clock train which alters the force on the detent upholding the weights.

The amplitude of the oscillation with this form of escapement can be found by equating $eh/(a+e)$ to the natural decrement of the arc per half period, and since this does not involve κ (except in the second order of small quantities) the amplitude ought to remain very constant, but the alteration of period due to the second term may be appreciable.

Both the dead-beat and gravity escapements owe such small variations in time-keeping as they are subject to, directly or indirectly, to variations in the driving force.

(19) In an escapement of which a model is now shown* this source of error

* The model referred to was exhibited at the May Soirée, 1911, but (owing to the limited time at disposal) not at the reading of the paper.

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does not exist, and it is hoped that with it variations of rate may be of a smaller order.

The pendulum carries a cross arm AB slightly above the level of the axis (fig. 9). From this arm three fine wires, C_1, C_2, C_3, one in the centre and one at each end, project downwards and terminate in a line passing at right angles through the axis of suspension. The centre wire dips always in a mercury cup D_2, and the end wires dip alternately in mercury cups D_1 and D_3, whose level is so adjusted that contact takes place near the end of each swing. The three wires are electrically connected, and hence a current can be transmitted alternately through the end cups to an electro-magnet.

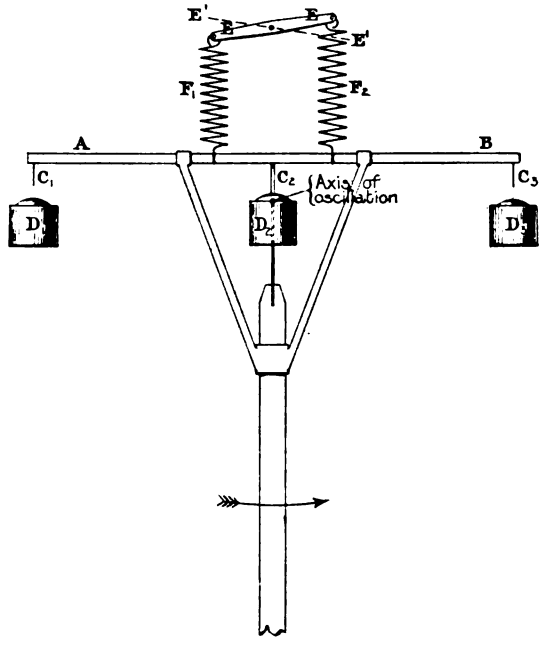

FIG 9.

In the present model the electro-magnet, through a kind of remontoir, works a short lever E whose axis is parallel to, and some distance vertically above, the axis of suspension. This lever can assume either of the two positions (E) or (E'), and takes these positions very rapidly when the current passes. At each end of the lever very fine spiral springs, F_1, F_2, descend and are connected below to the cross arm on the pendulum.

The forces acting on the pendulum are shown in fig. 10 by the thickened line.

Here E and E′ are the distances of the pendulum from the vertical at which the electric contacts are made. F and F′ are the changes of zero due to

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change of the mean force exerted by the springs when the lever shifts from one position to the other.

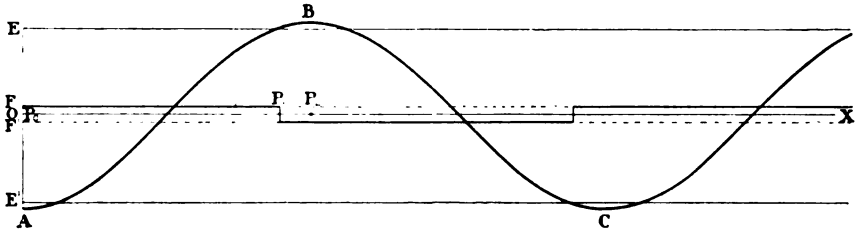

FIG. 10.

In fig. 11 let

$OP_0 = a_0$, $FP_0 = FP_1 = a_1$, $F'P_1 = F'P_2 = a_2$, $P_0FP_1 = \phi_1$, $P_1F'P_2 = \phi_2$,

then $$\phi_1 + \phi_2 = \pi - FP_1F'.$$

Let $$OE = OE' = h \quad \text{and} \quad OF = OF' = e,$$

then $FP_1F' = 2e\sqrt{(a^2-h^2)}/a$ and $a_2 = a_1 + 2eh/a_2 = a_0 + 4eh/a$.

Hence $$a_\pi = a_2 - e = a_0 + 2eh/a_0$$

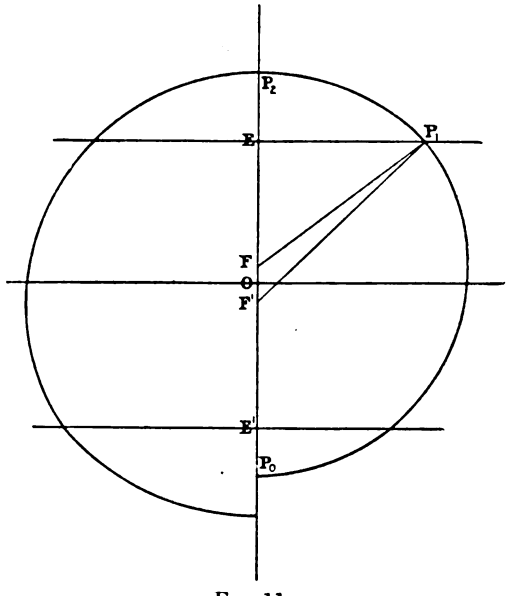

FIG. 11.

Thus, each half swing of the pendulum is quickened by $\tau e\sqrt{(a^2-h^2)}/\pi a^2$ and the amplitude (if there is no dissipation) at the same time increased by $2eh/a$.

The natural period of the pendulum is quickened by the action of the springs, whether the lever moves or not. Let L_0 be the unextended length of

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the springs and let the extension of both, when the lever is in its middle position, be L_1, also let w be the weight which will extend the springs to twice their natural length. Then if w is equal to the weight of the pendulum $\times q$, and r is the radius of the lever, the period, under the action of both gravity and the two springs, is $2\pi\sqrt{[\lambda/g(1+qL_1r/L_0\lambda)]}$.

The value of e in terms of L_0, q, r, and the extension ΔL of the springs caused by the movement of the lever from one extreme position to the other is $g\Delta Lrq/L_0\lambda$.

Thus the natural period of the pendulum is $2\pi\sqrt{[\lambda/(g+e\Delta L/L_0\lambda)]}$ and the alteration of this period due to the maintaining action of the escapement is $\tau e\sqrt{(a^2-h^2)}/\pi a^2$.

I have had no extended experience yet with this escapement. Its use in practice will depend on whether the mercury contacts can be made reliable.

Of the three escapements which have been considered the dead-beat is the only one in which there is no alteration of period except that depending on change of amplitude, but the amplitude changes quickly with change in the driving force, and the latter is liable to variations from causes which cannot altogether be avoided or eliminated.

In the gravity escapement if properly made the maintaining force is very constant and nearly independent of friction, but a change in the coefficient of friction, or of the pressure between the parts which have to slide while the weight is being released, may make a very appreciable difference in the rate.

In the escapement shown in the model the maintaining force is independent of friction,* but subject to a small change depending on the variation of the elastic coefficient of the springs with temperature. But if the material of the spring is properly chosen this is not important, especially as the spring force itself in this escapement is much smaller than the requisite maintaining force for the other two, because the only work to be done is to make up the natural loss of arc due to air resistance and yielding of the supports.

In order to show the order of errors of period due to the various sources mentioned, I subjoin examples computed for a "seconds" pendulum (*i.e.*, a pendulum with 2 seconds period, whose length is a little more than 39 inches) with a bob weighing 10 lbs. (corresponding to $21\frac{1}{2}$ cubic inches of mercury or 23 cubic inches of lead nearly). The other data, which are such as may be met with in actual clocks, are given as required.

(1) and (2) If the period is to remain constant to within $\tau \times 10^{-8}$ the length

* Except in so far as this may influence the time taken to shift the lever from one position to the other and thus to alter the phase at which the maintaining force is applied.

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must not vary by more than $7{\cdot}5 \times 10^{-7}$ inches or the effective gravitational force by more than $6{\cdot}6 \times 10^{-7}$ foot-seconds^2.

In connection with possible variation of the force of gravity it may be noticed that if the value of gravity at the earth's surface is increased in virtue of a general contraction of the earth, the length of the day, as measured by the pendulum, would remain unaltered, because the speed of the earth's rotation would be thereby increased in the same ratio as the frequency of the pendulum; and it is only by a comparison with some period unaffected by gravity (*e.g.*, the period of a mass on a spring) that the change could be recognised. A change of 10^{-8} in the absolute period of a pendulum would be produced by a shrinkage of only 2 inches in the radius of the earth.

(3) The radius of gyration of the bob must not vary more than $7{\cdot}9 \times 10^{-6}$ inch.

(4) If the arc of vibration is of 1° it must not vary by more than 1″ if the same constancy of period is to be maintained.

(5) The action of the suspension spring is twofold. In the first place it increases the stabilising force and thus acts to shorten the period, and secondly the effective length of the pendulum is shortened by $2nbc^3/3W$.

To get a numerical value for the shortening, assume that the suspension spring is subjected to a longitudinal stress of 20 tons per square inch by the weight of the pendulum, and that its width is $\frac{1}{2}$ inch. This gives 0·000334 inch for c, and we may take for steel $n = 3 \times 10^7$ lbs. per square inch.

With these data $\sqrt{(2nbc^3/3W)} = 0{\cdot}0104$ inch, which corresponds to a shortening of the period by 1 part in 7500.

(6) If a knife-edge suspension is used, the probable value of the radius may be anything from 0·003 or 0·002 inch down to the limiting value given by the strength of the material, and this radius has to be deducted from the effective length of the pendulum.

(7) If the knife-edge terminates in a flat surface 0·001 inch in width, the period of the pendulum whose arc of vibration is 1° is shortened by $\tau \times 4{\cdot}55 \times 10^{-6}$, and the smaller the arc assumed the greater will be the shortening of the period due to the flat.

The difficulty of ensuring a good cylindrical surface is a strong objection to the use of knife-edges.

(8) The stiffness of any given support can generally be found by tapping, and thus determining the pitch of the note given out by the natural vibration, care being taken that the natural vibration so caused is of the same type as the forced vibration which the oscillation of the pendulum would set up.

For the ordinary wooden case in which many standard clocks are

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mounted, this natural period may be as great or even greater than 1/50 second. When the pendulum is mounted on strong metal brackets fixed to masonry the period may be as small as 1/1000 of a second.

The corrections to the effective length in the two cases are 0·0039 inch for the period of 1/50 second and 0·000001 inch for the period of 1/1000 second.

On a seconds pendulum these would correspond to a difference of 5×10^{-5} and $1{\cdot}3 \times 10^{-8}$ seconds respectively between the actual period and the period of the same pendulum if rigidly supported.

(9) The effect of centrifugal force in altering the mean length of the pendulum may be just sensible.

We have for the maximum extension of the rod $4\pi^2\lambda a/nsgt^2$, and assuming that the suspension rod is steel and has a sectional area of 1/16 square inch, the other quantities remaining as before, viz., W = 10 lbs., λ = 39 inches, and arc of swing 1° (so that the linear amplitude a = 0·68 inch), the maximum variation of length is $3{\cdot}62 \times 10^{-7}$ inch, but the effect on the period, viz., $\tau \times$ half extension/2λ, is less than $\tau \times 10^{-8}$.

(10) For the calculations referring to the difference between the moment of inertia of a solid cylinder and an equal and similar volume of liquid, see Stokes, "Some Cases of Fluid Motion."*

With regard to the effect of temperature on the viscosity of mercury, I have no data. In any case, judging from Stokes' experiments and their difference from his calculated results, both points should be determined by suitable experiments rather than by a theory which does not take account of surface friction.

(11) As an example of the variation of period due to resistance varying as the velocity, suppose the natural decrease of arc to be such that the loss is 1/1000 part of the arc per swing, that is, the angle $\beta = 1/2000\,\pi$, then $\tau\beta^2/8\pi^2 = \tau \times 3{\cdot}2 \times 10^{-9}$, and is therefore negligible.

(13) (14) According to the investigations of Stokes† the sum of the effects of the buoyancy and inertia of the air on the period is equivalent to an increase of the mass of the pendulum, but not of its weight. For a cylindrical pendulum bob this increase is twice, and for a spherical bob one and a-half times, the mass of the air displaced, the extra mass being supposed concentrated at the centre of inertia, and not subject to gravitative attraction. That is to say, W = (not Mg, but) (M+$c\rho$V)g. In effect this is equivalent to diminishing the effective force of gravity by $c\rho$V or (if ρV = qM) by cq. If we take the density of the air as 1/800 and that

* 'Collected Papers,' vol. 1, p. 64, and the Supplement thereto, *ibid.*, p. 189; or 'Camb. Phil. Soc. Trans.,' vol. 8.

† 'Collected Papers,' vol. 3.

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of the pendulum as 10, $q = 1/8000$. For a cylinder $c = 2$, and the alteration of period due to the buoyancy and inertia of the air is $\tau q/g$ or $\tau \times 1{\cdot}25 \times 10^{-4}$.

(15) To this must be added the viscosity effect, which involves the absolute dimension of the pendulum.

It appears that for a cylindrical pendulum of the shape and dimensions assumed in these examples about 1/5 of the buoyancy inertia effect must be added to represent the frictional effect on the period.

(16) The other component of the viscosity effect acts on the amplitude and not on the period.

The total air effect therefore is to lengthen the period *in vacuo* by something like 1½ parts in 10,000.

There is no complete theory for the viscous flow round short cylinders. Stokes' theory is for spheres and for very long cylinders, but the ordinary pendulum bob is too short to make the flow over the ends of the cylinder negligible, and the true correction must be greater than that proper to a sphere and less than for an infinitely long cylinder.

Owing to variations of the barometer and thermometer, the density of the air may at times differ from the mean by about 1/20 part; hence, from air effects alone, the rate of the assumed pendulum may change by about 7½ parts in 1,000,000.

Escapements.

(17) In the dead-beat escapement it has been shown that the variation of rate is due to the variation of arc which must follow on variations of the coefficient of friction in the wheel work of the train, and, with regard to the latter, I have no data on which to form a calculation of a particular instance, but it appears almost certain, as may be seen by differentiating with regard to μ, the expression for the amplitude (on the supposition that f is proportional to the driving weight $\times (1-\mu)$) that the variation of amplitude is proportional to the variation of μ multiplied by some constant greater than unity.

(18) In the gravity escapement the variations of amplitude are small, but the variations of period due to the action of the escapement itself may amount to 10^{-6} for a variation of 1 per cent. in μ.

(19) In the model escapement friction does not enter, and the only source of variation of amplitude is the variation in the strength of the springs which may occur with variation of temperature and the possible variation of the phase at which the maintaining force is applied. Spring materials are now available, in which this alteration is almost insensible for such ranges of temperature as standard clocks are exposed to.

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Compensation.

(20) Much thought and ingenuity has been given to methods of compensating pendulums for the effects of varying temperature.

The chief effect to be compensated is the variation of the length of the pendulum. If an uncompensated pendulum has a steel suspension rod, the variation of length is 0·000012 (about 1/80000) inch per degree centigrade. Hence, for each rise or fall of 1° C., the clock will lose or gain about half a second a day.

The alteration of length and of the moment of inertia of the bob is not the only source of variation of rate depending on temperature, for elasticity of the suspension spring and the density of the surrounding air are also involved, but, as all the variations are directly proportional to the change of temperature, any form of compensation which will correct for variation of length may with a slight alteration be made to correct for the rest.

All the compensations actually employed have depended, in one way or another, on the use of bodies with different coefficients of expansion. In practice, the pendulum rod is either a compound structure (generally zinc and steel) of parallel strips or bars joined at the ends, whose lengths are so adjusted that the large expansion of the zinc compensates the smaller expansion of the steel, or the bob is a cylindrical chamber containing mercury, whose dimensions are determined so as to make the expansion of the mercury do the necessary compensation.

The compound suspension rod is free from one objection to which the mercury chamber is open, namely, that the suspension rod takes the temperature of the surrounding air more quickly than the large mass of mercury, thus causing a lag in the adjustment of the compensation.

I have found that it is convenient to compensate the pendulum rod independently of the bob, and to attach the latter to the rod at such a distance below the centre of inertia that the variation of the length of the pendulum thus caused when the temperature varies is just balanced by the variation of the moment of inertia.

Thus, taking $(h^2+\kappa^2)/\lambda$ as the length of the equivalent pendulum, make the suspension rod of a length $h+x$, and let the attachment of the rod to the bob be made at x. The rod is compensated so that $h+x$ remains constant at all temperatures, and this compensation can be verified in the laboratory with great accuracy.

The distance of the centre of inertia of the bob from the point of suspension becomes, when the temperature changes by Δt, $h-x(1+a\Delta t)$ and the radius of gyration becomes $\kappa(1+a\Delta t)$, where a is the temperature

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coefficient of the material of the bob, and, if we calculate x on the supposition that the equivalent length λ remains constant, we find $x = 2\kappa^2/h$. Thus x is independent of the coefficient of expansion of the material of the bob, and is a function only of its form.

With this arrangement the question of lag in compensation does not arise, at any rate in the first order of small quantities.

Materials (such as the alloy "invar" or melted quartz) are now available for suspension rods whose temperature coefficients are so small as to make special compensations for length unnecessary (the small outstanding expansions can be corrected by using a proper value for the x of the preceding paragraph), but these materials are not dense enough for advantageous use as pendulum bobs.

Airy first applied a compensation for the variation of the barometer. This was done by means of a magnet controlled by a float resting on the open mercury surface in the shorter leg of a syphon barometer. The movable magnet acted on another fixed to the pendulum, and, according to the height of the barometer, exercised a greater or less accelerating effect on the period. This compensation had to be adjusted by trial.

A simpler method is adopted in the model,* which has an additional advantage, in that it corrects for changes of density dependent on temperature as well as for pressure.

The whole pendulum and fittings are placed under a circular bell-glass, whose edge dips in a narrow, but deep, annular channel partly filled with mercury. Any change of density in the outer air causes the mercury to rise or fall on one side or other of the bell-glass, but, since the volume of the air within the glass is very large compared to the displacement caused by the movement of the mercury, the density of the air inside remains practically constant. The only variation of rate which the air can cause, except by variation of its density, is dependent on the change of viscosity with temperature, and this is small compared with the density effects.

In the particular case of the model, any change of external density is reduced to about 1/1000 within the bell-glass.

Considering the number of causes which may operate, especially in clocks with mechanical escapements, so as to vary the rate by quantities of the order of 1/1,000,000, it seems hardly likely that any device for maintaining the oscillation should ever secure a rate constant within 1/100,000,000. In particular, the maintenance of an arc of vibration constant to less than one second is hardly to be hoped for, for, even granting the maintaining force to be applied with perfection, the arc may vary in virtue of changes in

* The model referred to above (p. 517).

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the stiffness, etc., of the support, that is, on outside circumstances, whose changes can neither be avoided nor compensated.

On the whole, I think it seems probable better time-keeping might be secured by a properly designed balance wheel oscillating on a spring than by a pendulum. The balance wheel and spring has the great advantage of something like real isochronism, so that small variations of arc are unimportant, and I believe there is no good reason to consider the elastic constants of a spring kept at a uniform temperature or otherwise compensated are more liable to variation than the force of gravity.

The Effect of Temperature upon the Ductility of Zinc.

By W. B. Haines, B.Sc., Physics Research Scholar, University College, London.

(Communicated by Prof. F. T. Trouton, F.R.S. Received June 7; revised July 22, 1911.)

It is well known that zinc has the property of becoming soft at temperatures in the region of 150° C., while it is said to become hard and brittle at about 200°. This applies to the commercial variety of the metal, which always contains a small proportion of lead. These changes suggested an investigation into the effect of temperature upon the ductile properties of zinc, of which the present paper is a record.

The experimental plan adopted was the examination of the ductility of zinc wire at various temperatures. Wires about 15 cm. long were fixed in a vertical position in a bath of castor oil, and stretched by a weight applied to the upper end by means of a pulley. A cathetometer was used to measure the extension of the wire. At each particular temperature the rate of extension of the wire was calculated from the observations for several loads ranging up to the breaking stress.

The results of the work emphasize the importance of treating the wires in exactly the same manner in order to gain consistent results. Thus the state of the wire as indicated by the rate of extension under a given stress depends not only upon the temperature, but also upon other factors, such as the previous treatment which the wire has received. In order to gain the required consistency of result, the wires were prepared and used in the order of their position on the original hank of wire, so minimising the effect of any variation in condition along the hank. An endeavour was also made

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in obtaining a set of readings from each wire to maintain uniformity of treatment in all respects. The method of taking the readings was largely determined by the requirement that the behaviour of the wire should be investigated right up to the breaking point before an undue amount of stretching had introduced uncertain effects. This condition prevented the repetition of readings, which would otherwise have been desirable, as the flow of the zinc was not uniform.

Expression of Results.—The result of each experiment has been diagrammatically expressed by plotting the rate of extension per unit length R against the stress per unit* cross-sectional area S. Both R and S require a correction introduced by the stretch of the wire. In the calculation of R the mean length of the wire during the reading was used. The correction applied to S is made necessary by the diminution in diameter corresponding to the increase in length. It was made on the simple assumptions that the thinning is uniform, and that constant volume is maintained. Then if s be the extension and l the original length, the ratio of the applied stress to the corrected stress S is $1:1+s/l$. The suppositions involved here were tested by comparing measurements of the wires made before and after the experiments upon them. The comparison showed that any irregularities in diameter were about doubled by the stretching, and that the correction as applied to S was reliable to 0·7 per cent. These measurements also showed that differences between the diameters of different wires were small enough to be neglected. No correction was made for the very small friction of the pulley.

In this manner a curve was obtained for each temperature chosen over a range from 10° to 200° C. The results have been brought together by taking as a measure of the ductility the slope of the final portion of the curve corresponding to the particular temperature. In the case of a truly viscous flow, R and S are connected by a linear law, or $dR/dS = k$, where k is a constant proportional to the coefficient of viscosity. With such substances as pitch, which while approximately viscous in behaviour can yet be treated in the manner of the present experiments, k has been called the coefficient of viscous traction.† The behaviour of the zinc has thus been assumed to become approximately viscous toward the breaking stress. This assumption is justified by the results over a considerable range of temperature, and in any case the method gives a convenient and fairly accurate means of comparing the results. Fig. 1 gives a clear idea

* For the sake of convenience the unit taken was the initial cross-sectional area = 0·00581 sq. cm.

† Trouton, 'Roy. Soc. Proc.,' A, vol. 77, p. 426.

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of what is involved in the assumption. In the ideal case an abrupt change from the elastic to the viscous state is supposed, instead of the more gradual change which the real curve indicates.

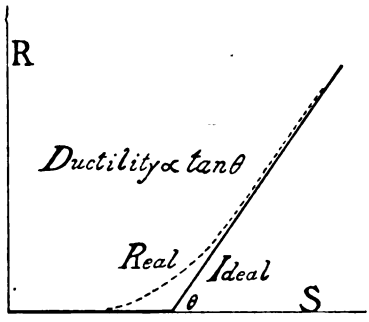

FIG. 1.

Results.—A preliminary experiment was first made upon a single wire under a constant load, the rate of extension being measured at intervals as the temperature rose from 70° to 150° C. The result showed two notable changes in the zinc over this range. Between 80° and 90° the metal becomes remarkably soft, as soft, in fact, as it is at 150°. At a few degrees above 90° a very definite hardening sets in, which has a turning point at about 115°.

Curves covering the whole range of the experiments are shown in fig. 2. These have been selected from a great number of perfectly consistent experiments, as being representative of the series. The experimental points

Temperature, 108° C.

Load.	Extension, per minute.	Length of wire.	Rate of extension.	Stress (corrected).
kgrm.	cm.	cm.		
3·0	0·032	16·2	0·0020	3·00
3·5	0·074	16·3	0·0045	3·52
4·0	0·121	16·4	0·0074	4·06
4·4	0·196	16·6	0·0118	4·51
4·6	0·246	16·8	0·0146	4·76
4·8	0·312	17·0	0·0184	5·03
5·0	0·368	17·2	0·0214	5·31

have been omitted from all the curves save three, in order to avoid confusion. These three, together with the table, give a sufficient idea of the experimental data upon which the results are based. The diagram shows curves for intervals of 20° between 50° and 200° C., except between 90° and 120°, where the interval is reduced to 10°. Below 50° the stresses involved are too large for the curves to be completed on this figure. An approximate idea of the behaviour at atmospheric temperature can be gained by taking the curve marked 122° and doubling the abscissæ.

The state of the zinc at any particular temperature is indicated both by the shape of the curve and by the position of the curve upon the diagram. The three curves 50°, 69° and 90°, show a regular increase in softness as the

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temperature rises, the form of the curves at the same time decreasing in curvature. At maximum softness the curve is practically a straight line, which indicates that a truly viscous behaviour is reached. At a few degrees above 90° a hardening of the zinc sets in, which is so rapid that, at 110°, the

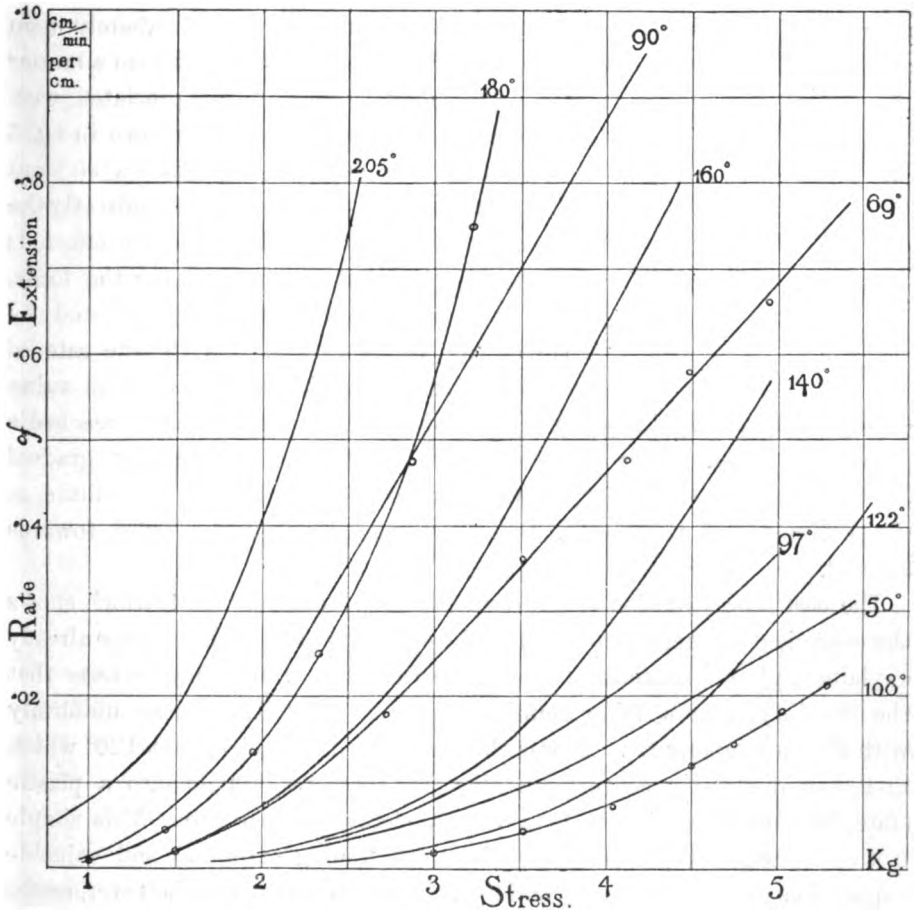

FIG. 2.

behaviour is comparable with that at 30°. There is, however, greater brittleness than at this lower temperature. From 110° onward there is a regular softening as the temperature rises. This certainly continues up to 200°, and one or two experiments above this temperature indicated that the softening continues at least up to 250° C. Although the zinc attains, at these higher temperatures, the same ductility as it shows at 90°, the character of the flow is different in the two cases. At the lower temperature, increase in softness corresponds to straightening of the curve, but at the higher

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temperatures the reverse is the case, for a regular increase in curvature is noticed as the temperature rises. The contrast is clearly shown in fig. 2 by the curves marked 90° and 180°. At 90° the wire can also be extended a greater amount, without breakage, than is possible at higher temperatures.

It is worthy of note that the hardening of the zinc which occurs in the region of 100° takes some time to develop. Thus the wire, immediately upon attaining this temperature, is soft, but after a short time it sets into a harder state. This fact was not at first appreciated, with the result that curves of the form shown in fig. 3 were obtained for experiments between 90° and 100°. Since the readings were started directly the wire was fixed in the bath, the time effect is superposed upon that due to changing the loads. This time lag was separately investigated by keeping the load constant. At 98° the rate of extension fell to one-eighth of its initial value during the first six minutes, at the end of which time the zinc had reached a permanent state. This effect of initial softening, followed by gradual hardening, is noticeable only between 90° and 120°. It is most definite at the beginning of this range, becoming smaller and more rapid towards the end.

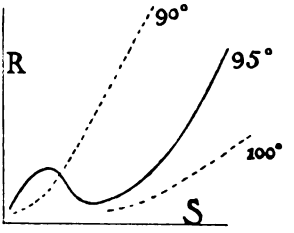

FIG. 3.

The best representation of the results is to be found in fig. 4, which shows the coefficient of ductility as calculated from each curve in the manner already explained, plotted against the temperature. It is interesting to note that the ductility, after a fairly definite change at 120° C., increases uniformly with rise in temperature. It was the discovery of this change at 120° which first showed, about a century ago, that zinc could be brought into a plastic state, by simply heating it to a very moderate temperature. This simple fact converted a little used metal into one finding extensive and valuable application in such trades as building. No previous notice, however, seems to have been taken of any peculiarity in the ductile properties of zinc at temperatures below 120°. Another noticeable feature of this diagram is that the softening which occurs toward 90° is as much a departure from the mean curve as is the hardening at 110°.

Discussion of Results.—The effect of the mode of treatment of the zinc upon its behaviour has already been mentioned. The effect of heating the wire to temperatures above 120°, and then cooling, is to diminish greatly its tenacity and ductility. This is due to the crystalline structure induced, as is shown by a microscopical examination of the fracture, and the change affects the behaviour at all temperatures when the wire is again heated. In

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this state the zinc does not show any of the peculiarities already explained. Its behaviour is very erratic, but shows on the whole a gradual softening as the temperature rises. In order to restore the ductility to the zinc all that is needed is to subject it to some such mechanical process as hammering.

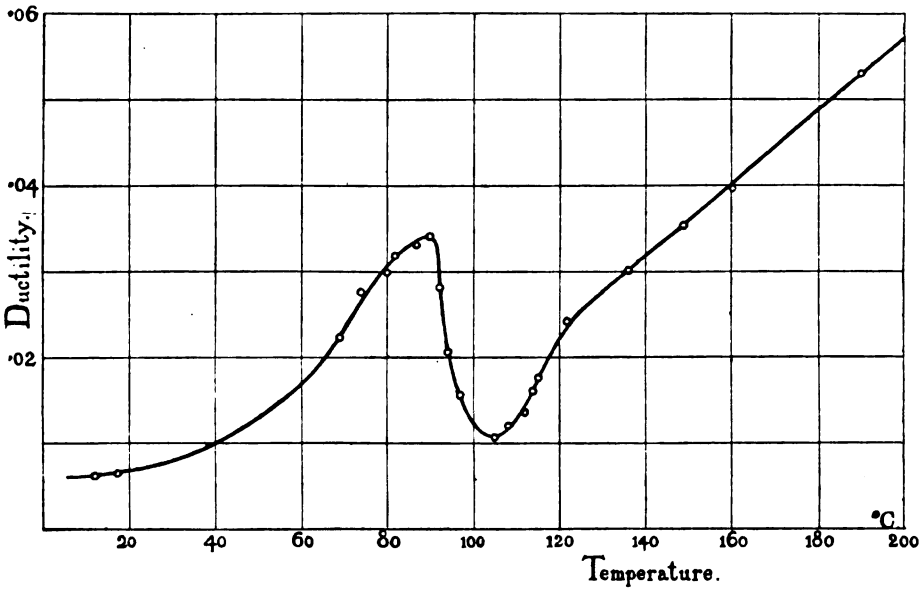

Fig. 4.

This crushes out the coarse crystalline structure, rendering the metal homogeneous and much more ductile. This was very marked in an experiment upon a small bar of zinc, which was hammered at a temperature of about 150° C., the test of its ductility being applied by flexure.

Considering how large is the number of factors which combine to determine the behaviour of the wire, and hence the form of the curves by which this has been represented, it will be seen that the curves have by no means as simple a physical meaning as their appearance would suggest. This explains why an endeavour to find a simple mathematical expression for them was not successful. More involved expressions could have been fitted, but their significance would be doubtful.

In all the experiments so far recorded ordinary commercial zinc was used, since this is the only kind obtainable in the form of wire. A careful analysis of the specimen used revealed the presence of 0·52 per cent. lead. It was thought to be desirable to know whether the peculiarity in the behaviour of this wire was due to the presence of lead, or to a true characteristic of zinc itself. The experiments could not be repeated with

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pure zinc, as it is impossible to produce wires of the pure metal. However, a comparison of the behaviour of the two forms of the metal was obtained by applying the method of flexure. A rectangular bar was sawn from a cast stick of pure zinc, and supported at either end in a small iron frame immersed in the oil bath. The precaution was taken of previously hammering this bar. Its rate of flexure under a force applied to its middle was then observed at different temperatures. In the case of commercial zinc a set of wires fixed side by side was substituted for the bar. These showed the same changes in the region of 100° C. as were observed in the experiments on stretching the wires, but, although these changes are so very marked, they could not be observed in the pure zinc. The bar showed a uniform softening as the temperature rose, the only peculiarity being a hardening in the region of 200°. Hence the evidence leads to the conclusion that the singularity observed in the ductility of zinc at temperatures in the region of 100° C. is produced by the admixture of a small proportion of lead.

In conclusion it is a pleasure to acknowledge my debt to Prof. F. T. Trouton and to Assistant-Professor A. W. Porter for constant encouragement and advice during the progress of these experiments.

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The Flame Arising from the Nitrogen-burning Arc.

By the Hon. R. J. STRUTT, F.R.S., Professor of Physics, Imperial College of Science, South Kensington.

(Received July 12, 1911.)

§ 1. *Introduction.*

Sir William Crookes was the first to draw attention to the flame arising from the high-tension alternating arc in air, and to point out that it was connected with the oxidation of nitrogen.* It was extensively used by Lord Rayleigh in connection with the isolation of argon, when I first had the opportunity of becoming acquainted with it. Of late years it has come into prominence in connection with the commercial manufacture of nitrogen compounds from the air, and is now within the purview of the electrical engineer.

Some investigations upon which I have recently been engaged have thrown considerable light on the processes occurring in this flame. The conclusions reached are not in agreement with some which have been expressed by other workers.†

§ 2. *The Arc in Pure Gases and in Air.*

If a Ruhmkorff coil or other form of high-tension transformer is supplied with alternating current in the primary circuit, an arc can be struck between the secondary terminals, which, for experimental purposes, are best made of platinum. A similar arc is obtained, using a continuous current interrupted by a Wehnelt or mercury turbine break. It is convenient to begin by considering the appearance of this arc in pure gases.

In hydrogen the discharge is observed to stretch straight across between the electrodes, without appreciably rising into an arch.

In pure nitrogen the phenomena are similar, except that the discharge tends to rise into an arch, particularly if the terminals are widely separated.

In pure oxygen an arch is also formed. In this gas the discharge has a bluish-white colour, and is much more diffuse than in the former ones. To a casual examination it may have somewhat the appearance of a flame; but the difference from the other pure gases is only one of degree. Close examination shows that there is nothing there but the true current-carrying arc itself.‡

* 'Chem. News,' 1892, vol. 65, p. 301.

† See, for instance, F. Howles, 'J. Soc. Chem. Industry,' 1907, vol. 26, p. 290.

‡ Compare Rayleigh and Ramsay, 'Phil. Trans.,' A, vol. 186, p. 219 (second paragraph).

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With air, an entirely new phenomenon makes its appearance. The arc is there as before, stretching from one terminal to the other, with a slight rise in the middle. But around, and more particularly above, it is an envelope of yellowish-green flame, which may rise to a considerable height above the arc, and terminates above in quite a sharp point, like a candle flame.

At atmospheric pressure the luminosity of the arc proper is so slight as to make it somewhat difficult to distinguish from the surrounding flame. The flame, however, gives no violet rays, while the arc is rich in these rays. Accordingly, the arc may be seen alone by examination through a deep violet glass, and then appears of about the same size and form as in pure nitrogen.

Fig. 1 shows a photograph of the air arc isolated in this way by a violet glass. Fig. 2 shows a photograph taken with an hour's exposure through a

FIG. 1.

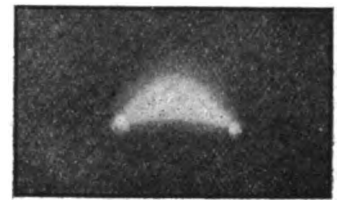

FIG. 2.

combination of green and yellow glass, which excludes the violet rays, but transmits the yellow and green ones in which the flame is richest. In this way a picture of the flame appears, without blurring by the intensely actinic glare of the arc proper. The photograph hardly brings out the pointed tip of the flame as distinctly as might be wished. This is probably due to the slight flickerings of the flame, inevitable during a long exposure.

The distinction between the arc and the flame may be made even clearer by another method, that of moderately reducing the air pressure. A rose-coloured arc is then clearly seen, quite distinct in colour from the surmounting yellow-green flame, and separated from it by a slight dark interval. Under these conditions it is quite obvious that the former alone carries the current (fig. 3). The flame, which does not appear in pure gases, is due to secondary causes which will appear in the sequel.

If we continue to reduce the pressure, and at the same time draw the electrodes further apart, the yellow-green flame expands. The phenomena become more conspicuous if, concomitantly with the reduction of pressure, the percentage of oxygen present is increased. Finally, the yellow flame fills the whole vessel, which none the less remains cool enough to allow the hand

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to be placed upon it. The flame remains visible for a moment after the arc has been switched off (fig. 4).

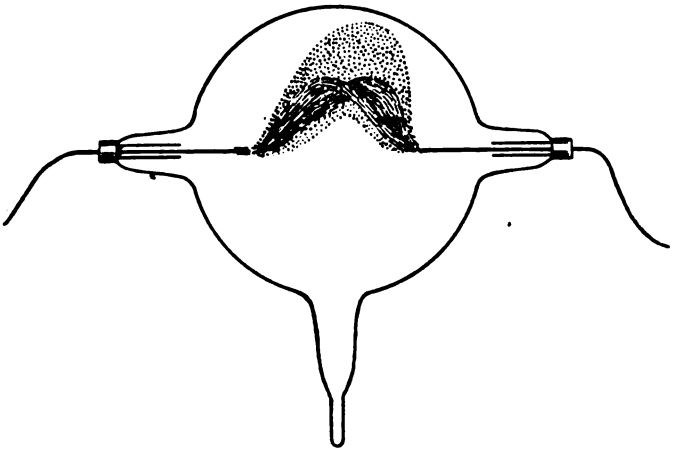

Fig. 3.

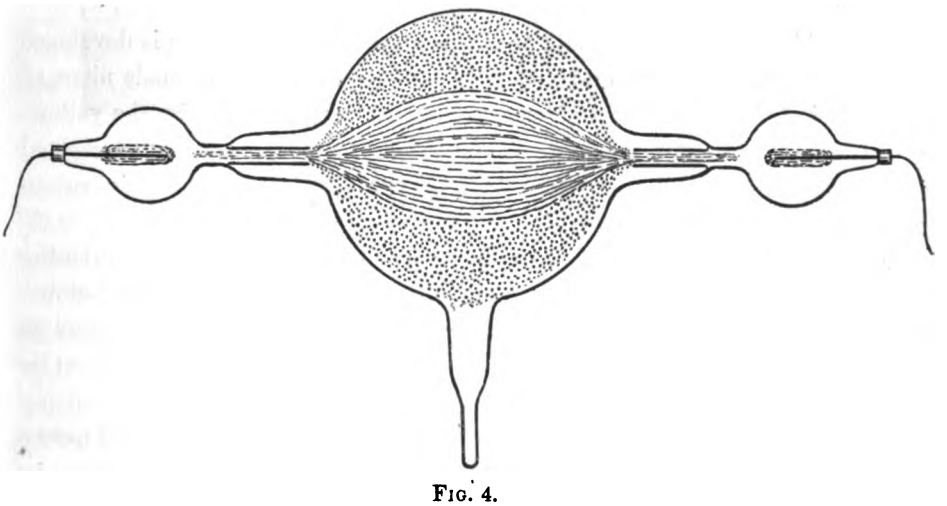

Fig. 4.

At this stage it is evident that the nitrogen flame is in no way distinct from the well-known "after-glow" sometimes observed in Geissler tubes filled with air*—a luminosity which persists after the discharge is over. This phenomenon I traced to its origin in a paper read before the Physical Society.† It will be convenient to briefly mention some of the experiments there described in detail.

* Not to be confounded with the glow due to active nitrogen, see 'Roy. Soc. Proc.,' A, 1911, vol. 85, p. 219.

† 'Phys. Soc. Proc.,' December 15, 1910, vol. 23.

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A current of rarefied air was drawn through a vacuum discharge tube by means of a power air pump. It remained luminous with the characteristic greenish-yellow light leaving the discharge, but this luminosity was destroyed by passing through silver wire gauze. Now, silver destroys ozone. It appears, then, that ozone is bound up with formation of the glow.

The greenish-yellow glow is not, however, observed in the absence of nitrogen. It was found that air deprived of the glow by silver gauze would glow again when more ozone was led into it. The air therefore contained some second ingredient necessary to the glow. This ingredient was concluded to be nitric oxide, formed by the discharge; and it was shown that the glow could be reproduced by leading ozone into nitric oxide, chemically prepared. It has been observed since that nitrogen peroxide gives the same result. The glow then is due to the further oxidation by ozone of oxides of nitrogen already formed in the arc. The arc supplies both ozone and nitrogen oxides, which combine, giving the greenish-yellow flame.

It is known that ozone will oxidise nitrogen peroxide to the pentoxide. When nitric oxide is led in, it is oxidised in two stages, first to peroxide, then to pentoxide. There is no doubt that the greenish-yellow flame is developed in the second stage; for I find that it is produced when ready-made nitrogen peroxide is fed into a stream of ozone. But if, as appears likely, the yellow-green luminosity is due to the nitrogen peroxide molecule, it may be evolved in the formation of that molecule from nitric oxide as well as in its subsequent further oxidation.

To sum up, the greenish-yellow flame from the high-tension alternating arc in air is shown to be in complete continuity with the "after-glow" phenomenon in vacuum tubes containing air. The latter can, by suitable experimental analysis, be proved to be due to the further oxidation of oxides of nitrogen by ozone. Accordingly it is concluded that the flame arising from the arc is due to the same cause. The arc produces ozone and oxides of nitrogen. These substances, independently produced, unite chemically in the region above and around it. The greenish-yellow flame is developed in the process.*

* It is right to mention that Muthman and Hofer, 'Ber.,' 1903, vol. 36, p. 440, express the opinion, for which, however, they do not offer any experimental evidence, that oxidation of NO proceeds in the flame. They do not mention ozone in this connection.

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Radiation in Explosions of Coal-gas and Air.

By W. T. David, B.A., B.Sc., Trinity College, Cambridge.

(Communicated by Prof. B. Hopkinson, F.R.S. Received May 24,—Read June 29, 1911.)

(Abstract.)

This paper contains the results of experiments on the radiation emitted by mixtures of coal-gas and air during explosion and subsequent cooling, carried out under the guidance of Prof. Hopkinson in the Engineering Laboratory at Cambridge. In the first part, measurements of the total radiation emitted by gaseous mixtures of various strengths and densities are given; and the second part consists of an investigation into the transparency and emissive power of the hot gaseous mixtures after explosion.

The gaseous mixtures were exploded in a plain cylindrical cast-iron vessel 30 cm. in diameter and 30 cm. in length, and were in all cases ignited by means of an electric spark in the centre of the vessel.

Into one of the end covers there was screwed a gunmetal tube which carried at its inner end a plate of diathermanous substance (a plate of fluorite was generally used), and behind it was placed a platinum bolometer with a blackened surface. The bolometer thus received all the radiation from the hot gaseous mixture which was transmitted through the plate of diathermanous substance. In order to measure the heat received by the bolometer its rise of electrical resistance was measured. The galvanometer, whose deflections were proportional to the rise of resistance of the bolometer, was of low period and carried a light concave mirror by means of which a spot of light was focussed on to a revolving photographic film rotating at a known speed, so that a continuous record of the rise of resistance of the bolometer, and therefore of the heat received by the bolometer, was obtained. At the same time and on the same film a continuous record of the pressure of the gaseous mixture was also taken by means of a Hopkinson optical indicator.

The following are the main results obtained from the experiments:—

Part I.—When mixtures of coal-gas and air of various strengths, at atmospheric density, are exploded in the vessel when its walls are blackened over with a thin layer of dull black paint—

(i) The total amount of heat lost by radiation to the walls of the vessel up to the moment of maximum pressure is roughly proportional to the

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product of the third power of the maximum absolute temperature attained into the "time of explosion."

(ii) The total heat lost by radiation to the walls during explosion and subsequent cooling is about 25 per cent. of the heat of combustion of the gas present in the vessel.

(iii) The emission of radiation in the initial stages of cooling after explosion is a function of the time from ignition as well as of the temperature. The emission varies very rapidly with the temperature and the time from ignition.

(iv) In weak mixtures (and probably also in strong mixtures) the rate at which radiation is emitted is a maximum some time before the attainment of maximum pressure, and probably occurs at the moment when the flame fills the vessel.

(v) Weak mixtures radiate much more powerfully in the initial stages of cooling after explosion than stronger mixtures do when they have cooled to the same temperatures as the weaker mixtures have in this epoch.

(vi) Carbonic acid gas emits radiation about twice as strongly as an equal volume of water vapour at the same temperature does.

In explosions of mixtures of the same strength, but of various densities—

(vii) The total heat lost by radiation per cent. of the heat of combustion of the gas present in the vessel up to the moment of maximum pressure decreases as the intensity increases.

(viii) Denser mixtures emit radiation much more strongly than thinner mixtures—especially at the moment of maximum pressure and in the initial stages of cooling; the emission varies approximately as the square root of the density.

Part II.—The following results refer to experiments made in a vessel of the same dimensions, whose walls were silver plated, and therefore could be made reflecting or absorbent at will. The experiments were made with the bolometer placed at some distance behind the plate of fluorite, so that the emission was measured from a cone of gas of small solid angle.

(ix) The intrinsic radiance from a gaseous mixture at any given temperature after explosion depends largely on the reflecting power of the interior surface of the explosion vessel, and also on the size of the vessel. The greater the reflecting power, or the greater the size of the vessel, the greater the intrinsic radiance. This effect is probably due both to greater vibratory energy and to greater transparency of the gas in the larger vessels and in the reflecting vessels.

(x) (*a*) Gaseous mixtures, after explosion in a vessel with reflecting walls,

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are very highly transparent to the radiation which they emit at maximum pressure and throughout cooling.

(*b*) Gaseous mixtures, after explosion in a vessel with black walls, are very highly transparent at the moment of maximum pressure, and also in the initial stages of cooling. Later on in the cooling they become fairly opaque.

[(xi)–(xiv) refer to coal-gas mixtures of the same strength but of different densities.]

(xi) The ratio of the intrinsic radiance from a definite thickness of gaseous mixtures of the same strength at any given temperature when the walls of the explosion vessel are reflecting to that when the walls are black decreases as the density increases.

(xii) When the walls of the explosion vessel are black, the transparency of a thickness of gas inversely proportional to the density at any given temperature increases as the density increases.

(xiii) (*a*) The intrinsic radiance from a definite thickness of gaseous mixture at any given temperature, after explosion in the vessel with black walls, varies as the square root of the density.

(*b*) The intrinsic radiance from thickness of gas inversely proportional to the density varies as the fourth root of the density.

(xiv) The intrinsic radiance corrected for absorption from 1/D cm. of the gaseous mixtures at any given temperature in the vessel with black walls seems to decrease as the density (D) increases.

(xv) The radiation (after correcting for absorption) from the hot gaseous mixture after explosion varies with the temperature approximately as Planck's formula for a single wave-length of $3{\cdot}6\,\mu$; this at high temperatures (1800° C. to 2400° C. abs.) varies approximately as the square of the absolute temperature.

Many of the above results may be explained in terms of the following theory: A molecule, as it describes its free path, loses energy owing to the emission of radiation, and gains energy owing to the absorption of energy from the ether, and the vibratory energy of the molecule will increase or decrease according as the absorption is greater or less than the emission. During collision with another molecule, there will be a transference of energy between the vibratory energy and the rotational and translational energies, which, as Mr. Jeans has shown, will be very rapid if the duration of collision is comparable with the periods of vibration of the molecule. In the case of CO_2 and steam at high temperatures, the duration of collision between the molecules is probably short in comparison with the periods of their low-frequency vibrations, and the vibratory energy of the molecules

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will therefore tend to take up during collision a value such that the energy in each of the vibratory degrees of freedom equals that in each of the rotational and translational degrees. During collision, therefore, the vibratory energy of the molecules will tend to take up a value which is proportional to the absolute temperature, but, during the free path, there may be considerable departure from this value if the energy density in the ether is above or below a certain value, and the time of description of free path is not very short. The average value of the vibratory energy of the molecules will therefore depend not only upon the temperature of the gas, but also upon the value of the energy density in the ether, the rate at which the molecules emit radiation, the time of description of free path (inversely as the density of the gas), and the rate of partitioning of energy during collisions.

From result (iv) above, it is highly probable that the violence of combustion during explosion causes a considerable part of the energy of combustion to pass into the form of internal vibrations of the carbonic acid and steam molecules. Part of the energy in these vibrations is lost by radiation, but the greater part is transformed into rotational energy and translational or pressure energy.

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The Heating Effect of the Currents in Precise Measurements of Electrical Resistance.

By R. T. Glazebrook, F.R.S., W. R. Bousfield, K.C., and F. E. Smith.

(Received July 29, 1911.)

(From the National Physical Laboratory.)

In a paper on the specific heat of water,* one of us describes an experiment in which the passage of a current of 4·4 ampères through an oil-cooled manganin resistance of 1·2-mm. wire produced an increase in the resistance corresponding to an increase of temperature of 60° C. As the cooling surface of the resistance was 16 sq. cm. per watt, such a large increase of temperature was thought to be improbable, and the change of resistance was attributed to some other cause. However, the effect of the passage of the current was similar to that resulting on raising the temperature, and, because of this, it was proposed to call the change a *thermoid* effect. With platinum wires similar results were obtained, the increase of resistance being nearly proportional to the square of the current and inversely proportional to the radius of the wire.

The change of resistance with varying current was investigated by Dr. E. H. Griffiths in 1893.† Using a fine platinum wire, he found the increase of resistance to be proportional to the square of the applied voltage. With regard to this increase, Dr. Griffiths remarks:—"It seemed absolutely immaterial whether the current was on for only a few seconds or indefinitely." Previous experiments on an alloy of copper, manganese, and nickel had shown that the resistance of the alloy changed appreciably in the course of one and a-half hours when a current of ½ ampère was passed through it, and Dr. Griffiths states that the rise appeared to be a function of the current rather than of the time. If, in Dr. Griffiths' determination of the mechanical equivalent of heat, he had neglected the rise of resistance of the wire with increasing current, an error of about 1 part in 60 would have been introduced.

The question as to whether the rise of resistance is due entirely to increase of temperature or due in part to some other effect of the current is of extreme importance for precise electrical measurements. Moreover, since in many measurements it is necessary to use large currents, it is desirable to

* "The Specific Heat of Water and the Mechanical Equivalent of the Calorie at Temperatures from 0° C. to 80° C.," 'Phil. Trans.,' A, vol. 211, pp. 199—251.

† 'Phil. Trans.,' A, 1893, pp. 361—504.

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have some easy means of calculating the resistance for any current which may be used.

The change of resistance due to the heating effect of the current may be calculated if the temperature coefficient of resistance and the thermal emissivity are known. Our experiments show that the thermal emissivity is a function of the temperature of the wire, but for a small range of temperature the change is small. If we take the mean emissivity over a range of temperature not greater than 40°, the rise of temperature due to a current may be calculated with a fair degree of accuracy by means of equation (2) which follows, it being assumed, of course, that the rise does not exceed 40°.

If R = resistance of wire, L = its length in centimetres, r = its radius in centimetres, C = current, θ = difference of temperature between the wire and its surroundings when a steady temperature results, h = mean thermal emissivity of the surface in calories per second, J = Joule's equivalent, we have

$$C^2R/J = 2\pi rLh\theta, \tag{1}$$

or

$$\theta = 0{\cdot}038\,C^2R/Lrh. \tag{2}$$

The maximum variation of temperature over a cross-section of a wire has been shown by Dr. A. Russell* to be $\rho\,C^2/16{\cdot}8\,\pi^2KR^2$ where ρ is the specific resistance and K the thermal conductivity. In the case of the manganin coil used at Hendon, $\rho = 4\times10^{-5}$ and we may take K = 0·1, so that for a current of 5 ampères the difference of temperature between the axis and outer skin of the wire was of the order of 0°·016 C. In all that follows, we assume, therefore, that over a cross-section of a wire the temperature is uniform and that no strain is likely to occur because of the temperature gradient.

The usual form of expression for the change of resistance with temperature of a resistance wire is

$$R_t = R_0(1+\alpha t+\beta t^2), \tag{3}$$

where α and β are constants.

When the surroundings of the wire are maintained at a constant temperature and a current C is passed through it, the temperature of the wire is raised, and it follows from (2) that its resistance may be written in the form

$$R_{(C')} = R_0[1+\alpha(aC^2)+\beta(aC^2)^2], \tag{4}$$

where $a = 0{\cdot}038\ R_{(C')}/Lrh$, and α and β have the same values as before.

If there be some other effect of the current which increases the resistance,

* 'Theory of Electric Cables and Networks,' p. 216.

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then an additional term must be added to (4), which would be of the form γC^2, where γ is a constant.

To decide whether or not this is so, we must be able to calculate a, which involves a knowledge of the thermal emissivity. The most direct way of determining the latter is to measure the temperature of the wire while the current is passing through it. Such a measurement could not be made by means of thermo-junctions, as any arrangement of such would not only alter the conditions of cooling near the junction, but it might also be equivalent to increasing the diameter of the wire. One of us has shown that in the case of mercury resistances the temperature and resistance can be measured simultaneously, forming a very convenient mercury-resistance thermometer. The temperature is measured by the expansion of the mercury, and the temperature of a wire can be measured in a very similar way. Our arrangement for measuring the expansion is shown in fig. 1.

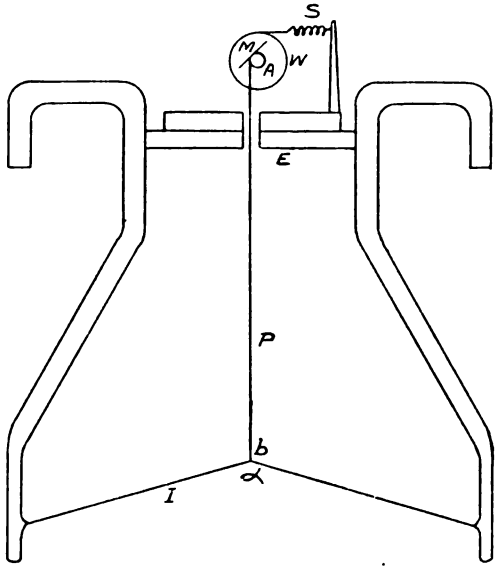

FIG. 1.

The wire experimented with was of iron; it was 12·4 cm. long, 0·02 cm. in diameter, and had been carefully annealed by passing a comparatively large current through it for one hour, the current being then gradually diminished in value so as to ensure slow cooling.

The wire I is connected to two copper leads and is stretched taut by means of a phosphor bronze wire P which passes over an axle A, 4 mm. in diameter. The wire passes round the axle three or four times and is then soldered to it. The wheel W is 1½ cm. in diameter and the spring S ensures

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that the wires are always stretched taut. A small mirror M is secured to the axle and reflects a beam of light so as to produce an image at a distance of 1 metre. E is an insulating support of ebonite.

When I increases in length, P is pulled upwards, and the amount by which the point b is raised is optically magnified about 1000 times. In general, the amount by which b is raised is greater than the increase of length of I. If the angle α is nearly 180° the mechanical magnification is considerable. However, we found it more convenient to make α about 150°, in which case the mechanical magnification is about 2. Our estimate of the total magnification was 2000, which means that for the 12·4 cm. length of wire we used, an increase of temperature of 1° should produce a deflection of 2·6 mm.

The apparatus was calibrated by immersing it down to the point b, first in cold and afterwards in hot water. The wire quickly took up the temperature of the water and the remainder of the apparatus was regarded as constant in temperature. The results are given in Table I.

Table I.—Calibration of Temperature Scale.

Temperature of wire.	Difference of temperature.	Scale readings.	Difference of scale readings.
°C.	°C.	mm.	mm.
11		63	
	40		84
51		147	
11		60	
	39		78
50		138	
11		39	
	50		105
61		144	
11		38	
	48		105
59		143	
Sum	177	—	372
	Thus 1° is represented by 372/177 = 2·1 mm.		

The means thus devised of measuring the temperature of a wire during the passage of a current through it rendered it easy to measure its resistance and temperature for any value of the current. The change of resistance with temperature could be determined by a separate series of observations and the validity or invalidity of equation (4) established.

It was of course important to ensure that in any method adopted for measuring the resistance of the wire the other resistances involved did not change, or, if so, changed by known amounts. Dr. E. H. Griffiths, in the paper already referred to, describes several arrangements for measuring the

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change of resistance with increasing current. Another arrangement, in which a mercury-resistance thermometer is employed, has also been described by one of us and has been used in making the observations at Hendon. Fortunately, at the National Physical Laboratory such standards of resistance are in use as enable a simple Wheatstone bridge to be used with manganin resistances in three of the arms, of such dimensions as to exclude error from the cause mentioned.

In general, the bridge consisted of two ratio coils of manganin, having nominal values of 10 and 1000 ohms respectively, a heavy current manganin standard of 0·01 ohm, and the wire under observation. All of the resistances were immersed in a bath containing 7 gallons of well-stirred paraffin oil maintained at a constant temperature of 15° or of 20° C. When a balance was obtained (by shunting the 10 or 1000 ohms coils) the same current passed through the 0·01 ohm and the wire (usually of 1 ohm resistance), and since, in all of our measurements, the current density in the 0·01 ohm standard was small, we assumed there to be no appreciable change in the resistance of this standard. The results of our observations show that we were justified in assuming this, but as a check we also used ratio coils of 10 and 10,000 ohms, and a heavy current manganin standard of 0·001 ohm in series with the wire. When the wire had a nominal resistance different from 1 ohm the 10,000 ohms was replaced by a variable resistance.

At the same time as the resistance was measured the temperature of the wire was indicated by the deflections of the spot of light. For values of the current less than 1 ampère no readings of the deflection were taken; for higher currents several readings were taken, as it was found that the errors of observation might amount to three or four degrees. The values of C, C^2, R, and the increase of temperature (θ) of the wire as thus recorded are given in Table II.

Table II.

C.	C^2.	R.	Deflection in mm.	Mean deflection = d.	$\theta = d/2{\cdot}1$.
					° C.
0·2	0·04	0·5760			
0·5	0·25	0·5795			
1·0	1·0	0·5920	19, 16, 16, 12, 14	15	7
1·125	1·27	0·5965	16, 20, 15, 14, 17	16	8
1·5	2·25	0·6127	33, 37, 42, 40, 35	37	18
2·0	4·0	0·6420	54, 61, 50, 64, 56	57	27
2·5	6·25	0·6790	97, 110, 106, 98, 103	103	49
3·0	9·0	0·7255	135, 138, 129, 140, 130	134	64
4·0	16·0	—	247, 241, 250, 247, 234	244	116

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Afterwards the change of resistance with temperature of the wire was determined, and these results are plotted on the chart (fig. 2). If, when a current is passed through a wire, the rise of resistance is due to the heating effect only of the current, then for a given resistance the temperature as deduced from the resistance-temperature chart should agree with that obtained from the expansion of the wire. Table III gives the rise of temperature obtained in the two ways.

Table III.

C.	C^2.	R.	θ as given by		Difference.
			Resistance-temperature chart.	Expansion of wire.	
			° C.	° C.	
1·0	1·0	0·5920	7·3	7	−0·3
1·125	1·27	0·5965	9·3	8	−1·3
1·5	2·25	0·6127	16·4	18	+1·6
2·0	4·0	0·6420	29	27	−2
2·5	6·25	0·6790	46	49	+3
3·0	9·0	0·7255	66	64	−2
4·0	16·0	—	—	[116]	
		Sum.....	174	173	−1

The values of θ obtained in the two ways being in such close agreement, and the small differences being sometimes positive and sometimes negative, we conclude that the heating effect of the current was the sole cause of the observed increase of resistance. However, we think it desirable to add that when electrical measurements are made with wires not carefully annealed, the passage of a current through them does often produce permanent changes in the resistance. In addition, therefore, to raising the temperature of a wire, a current may so alter the molecular structure as to change, temporarily or permanently, the specific resistance. Very similar effects may be produced by a cycle of temperature, and it is at present difficult to say whether or not the change in the specific resistance is due entirely to the change of temperature of the wire. With well-annealed wires the changes are small.

It is now possible to calculate h, the thermal emissivity of the surface of the wire. For the iron wire experimented with this increases with the temperature, the values being as follows:—

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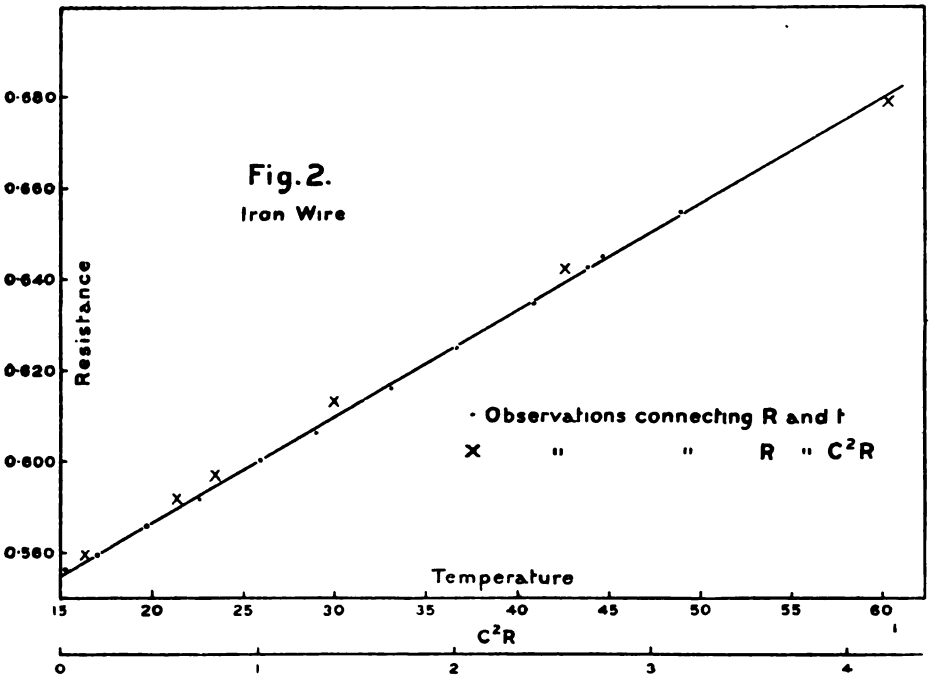
Temp.	h.	Temp.	h.
°C.		°C.	
15 + 7·3	0·025	15 + 29	0·027
9·3	0·025	46	0·028
16·4	0·026	66	0·030

On the diagram (fig. 2) the values of R and C^2R have been plotted in addition to the values of R and temperature, the scales of temperature and C^2R being so chosen that for all practical purposes a single curve connects R and t and R and C^2R. If R and C^2R/h are plotted the resulting curve may be made identical (by suitably choosing the scale of C^2R/h) with that connecting R and t.



The above-described experiments with the iron wire having established the fact that the increase of resistance is substantially due to the increase of temperature, we give the results of some measurements on other wires.

In two of our experiments fuse wires were used. The resistances, lengths, and radii of these were measured, and the melting points were determined in hot glycerine. Portions of the wires were then placed in an electric circuit, and the current gradually increased until they fused. This

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was done in air as well as in well-stirred paraffin oil. The results are as follows:—

	Wire No. 1.	Wire No. 2.
Length	27 cm.	18 cm.
Radius	0·01 cm.	0·016 cm.
Resistance	1·0 ohm	0·25 ohm
Melting point	183° C.	226° C.
C in air	1·36 amp.	2·6 amp.
(Mean) h in air	0·0015	0·0018
C in oil	6·1 amp.	17·3 amp.
(Mean) h in oil	0·031	0·080

In the case of wire No. 2 the melting point is above that of the boiling point (190° C.) of the oil used. This may explain the large mean value of h in oil. These experiments show clearly that very large temperature differences between the wire and the oil may exist, even with a well-stirred bath.

Other experiments were made with wires of manganin and of platinum silver, and curves were plotted connecting resistance and temperature and resistance and C^2R. When the scale of temperature was suitably chosen the resistance-temperature curve was in each case practically coincident with the resistance-C^2R curve. The mean value of h was of the order 0·03.

The experiments hitherto recorded were made at the National Physical Laboratory. We now come to others, most of which were made at Hendon.

Observations were made on pairs of wires of similar materials, No. 1 of each pair being about 0·03 cm. diameter and No. 2 being about 0·02 cm. in diameter. The wires were bare and immersed in well-stirred paraffin oil, the current being gradually increased from 0·1 to 3 ampères. In the case

Table IV.

Current.	Silver.		Copper.		Aluminium.		Nickel.		Iron.	Platinum.	
	No. 1.	No. 2.	No. 1.	No. 2.	No. 1.	No. 2.	No. 1.	No. 2.	No. 2.	No. 1.	No. 2.
0·1	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
0·2	1·0000	1·0000	1·0002	1·0000	1·0000	1·0000	1·0000	1·0000	1·0001	0·9998	1·0005
0·5	1·0001	1·0000	1·0004	1·0000	1·0002	1·0003	1·0002	1·0009	1·0015	0·9996	1·0022
1·0	1·0005	1·0008	1·0007	1·0010	1·0008	1·0019	1·0020	1·0057	1·0075	1·0001	1·0093
1·5	1·0012	1·0023	1·0013	1·0026	1·0021	1·0044	1·0049	1·0138	1·0174	1·0008	1·0209
2·0	1·0023	1·0047	1·0019	1·0049	1·0038	1·0080	1·0093	1·0253	1·0327	1·0019	1·0379
2·5	1·0036	1·0075	1·0028	1·0078	1·0057	1·0136	1·0148	1·0399	1·0521	1·0034	1·0590
3·0	1·0052	1·0110	1·0040	1·0116	1·0083	1·0190	1·0216	1·0623	1·0781	1·0051	1·0856
3·5			1·0052							1·0073	1·1205
4·0			1·0068							1·0098	1·1578

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of the platinum wires and of one copper wire, currents of 3·5 and 4 ampères were also employed. Table IV gives the comparative resistances, the temperature of the bath being practically constant.

For all of the above, curves connecting C^2R and the resistance have been plotted and in all cases practically straight lines result. The temperature coefficients of resistance are given in Table V and these, together with the resistance-C^2R curves enable the relation between θ, the rise of temperature, and C^2R to be found. The mean value of h for the range of temperature θ has been calculated from the equation

$$h = 0{\cdot}038C^2R/Lr\theta,$$

where L is the length of wire having a resistance R.

In Table V we give the diameters of the wires, the temperature coefficient of resistance, the resistance per unit length at 20° C., and the mean value of the thermal emissivity.

Table V.

Wire.	Diameter.	Approximate temperature coefficient of resistance at 20°.	Resistance per centimetre at 20°.	h.
Silver, No. 1	0·0305	0·00370	0·00229	0·037
„ No. 2	0·0200	0·00352	0·00523	0·058
Copper, No. 1	0·0303	0·00390	0·00243	0·054
„ No. 2	0·0199	0·00392	0·00564	0·066
Aluminium, No. 1 ...	0·0302	0·00402	0·00399	0·044
„ No. 2 ...	0·0200	0·00407	0·00898	0·067
Nickel, No. 1	0·0303	0·00446	0·01283	0·061
„ No. 2	0·0200	0·00445	0·02941	0·076
Iron, No. 2	0·0200	0·00400	0·0465	0·088
Platinum, No. 1	0·0505	0·00394	0·00484	0·051
„ No. 2	0·0173	0·00394	0·0417	0·082

It will be observed that h is greater for the small wires than for the larger ones; we have already seen that it increases slightly with the temperature. The mean value 0·062 is about twice that observed at Teddington with wires of iron, manganin, and platinum silver. The cause of this may be partly due to a difference in the paraffin oils, but we believe it to be principally due to the fact that much more vigorous stirring is employed at Hendon.

The importance of uniform stirring must not be overlooked. Dr. E. H. Griffiths tried the effect of variations, and found, as would be expected, that the more perfect the stirring the less the wire became heated, but within the limits of stirring employed in his experiments on the mechanical equivalent of heat, no correction was thought to be necessary.

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In the case of copper wire No. 1, the following results were obtained with a current of 3 ampères:—

	Resistance.
Normal stirring	1·0038
Very vigorous stirring	1·0027
No stirring	1·0173

These figures seem to show that the normal stirring employed at Hendon was vigorous, and that the value of h resulting from such stirring is as great as would be likely to be realised in ordinary practice with bare wires immersed in paraffin oils.

In the case of wires covered with silk and shellac, the heating effect is greater than with bare wires, and is best found experimentally by measuring the variation of resistance with temperature and of resistance with current.

We now briefly indicate the importance for precise electrical measurements of the heating effect of the current.

For such electrical measurements as those involved in the determination of the mechanical equivalent of heat, it is clearly of importance, especially when coils with large temperature coefficients of resistance are used.

Dr. E. H. Griffiths, who employed a platinum wire for the heating, allowed for this change of resistance, and pointed out the importance of determining the resistance for various currents.

In Dr. Barnes' determination of the mechanical equivalent the current was measured by measuring the potential difference on a coil of platinum silver through which the current flowed. This coil was immersed in well-stirred oil, and Dr. Barnes believed the increase of temperature of the wire to be less than 0·1° C. While this may be possible, it is of interest to point out that in Dr. Barnes' experiments the maximum current which passed through one platinum-silver wire was 1 ampère. Each wire was about 100 cm. long, 0·02 cm. radius, and 4 ohms in resistance. If these values are substituted for C, L, r, and R in equation (2), we find that θ, the rise of temperature, is equal to $0{\cdot}076/h$. If the cooling effect of the stirring was the same as at the National Physical Laboratory (*i.e.*, if $h = 0{\cdot}03$), the value of θ is 2°·5, equivalent to an increase of the resistance of 6 parts in 10,000. If, on the other hand, the cooling effect of the stirring corresponded to the most vigorous stirring set up at Hendon, the rise of temperature would be 0°·95 C., equivalent to 2·4 parts in 10,000 of the resistance.

For the comparison of standards of resistance the heating effect of the current is sometimes overlooked, especially when a comparison of methods is made.

For instance, it is generally thought that in bridge methods for the

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comparison of resistance much larger currents can be used than in the potentiometer method, because in the bridge methods the currents pass through the resistances for a few seconds only. In general, however, this is a mistake, for the temperature of a resistance coil in oil rises to within a tenth of a degree of the maximum temperature within a few seconds of the circuit being closed.

If the maximum increase of temperature of the wire is θ_1 and if θ is the increase of temperature t seconds after making the circuit, we have

$$\log_e \theta_1 - \log_e (\theta_1 - \theta) = 2ht/\Delta r S, \qquad (5)$$

where Δ is the density of the material of the wire, and S is the specific heat.

Experiments were made on a manganin wire 0·6 mm. in diameter, and the resulting values of h were 0·00115 in air and 0·021 in oil. The value of Δ S was about 1·0. For a current of 1·5 ampère the maximum elevation of temperature of the wire in air was 38°, the actual temperature being 20°+38° = 58°. By means of equation (5) we have calculated the time in seconds, after closing the circuit, corresponding to various values of $\theta_1 - \theta$. The times and temperatures of the wire are given in Columns 1 and 2 of Table VI. As a check on these values we measured the change of resistance of the coil (by observing the galvanometer deflection) during the first minute of the passage of the current of 1·5 ampère, and from the resistance values we estimated the temperature with the aid of a resistance-temperature chart. These times and temperatures are recorded as "observed" values, and are given in Columns 3 and 4.

Table VI.

Current = 1·5 ampère. Maximum temperature = 58° C.

Calculated.		Observed.	
Time.	Temp.	Time.	Temp.
secs.	° C.	secs.	° C.
15	46	12	46
18	48·5	20	48·5
20	50	24	50
25	52·5	27	52·5
28	53·5	33	53·5
35	55·5	37	55·5
47	57	50	57

In oil a current of about 6·4 ampères was required to raise the temperature to 58°, but since $2h/\Delta r S$ is about twenty times the value in air, the rate of increase of temperature is much greater. The final temperature of 58° is reached within 0°·1 in less than 5 seconds after closing the circuit.

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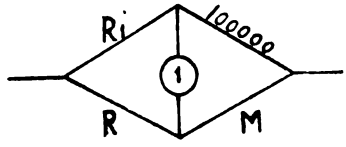
APPENDIX.—By W. R. BOUSFIELD, K.C.

(Received September 20, 1911.)

It is a matter of interest to determine the exact relation of the actual effect to the radius of the wire, but the experiments previously described were not sufficiently comparable *inter se* to enable this to be done. Differences in stirring produced notable differences in the results, and even differences in the winding of the wire on the mica plate were material. To bring these variable elements under control, the wire was soldered to two heavy copper electrodes and lightly stretched longitudinally in a glass tube, through which flowed a current of cooling water. Owing to the velocity of the water and to the fact that the wire was led into and out of the main tube by side tubes at right angles, the flow was necessarily turbulent. Some transverse vibration of the wire produced by the water current also tended to prevent mere gliding flow. The diameter of the tube was 0·97 cm. and the rate of flow (except in one experiment) was 100 c.c. per second, giving a mean velocity in the direction of the length of the tube of about 135 cm./sec. In the subjoined experiments the wires used were the soft platinum wire of 0·0505 cm. diameter which had been used for a previous experiment in the stirred oil bath, and a series of smaller wires drawn from a portion of the same wire so as to be completely comparable as regards material.* The figures for the experiment on the first wire of the series are given below. In the bridge arrangement, R, the resistance to be measured, was in series with a mercury



thermometer resistance M, and the other arms of the bridge consisted of manganin resistances, one of 100,000 ohms and the other, R_1, adjustable. A current of 5 ampères was passed through the wire for an hour before taking the measurements. The second column in the table records the value of $C^2 \times 25$ as determined by an ampère balance in the circuit, the accuracy of which could be relied upon within 1 in 5,000. The temperature of the inflow water during the experiment was 20·85° C. The length of the wire was 24·5 cm. The resistance of the column of tap water in the tube between the thick copper electrodes (measured by means of the Kohlrausch

* Our best thanks are due to Messrs. Johnson and Matthey, who were kind enough to give special attention to the drawing of the various wires required for the purposes of the investigation.

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wheel-bridge and telephone before soldering in the wire) was 82,000 ohms, *i.e.*, about 600,000 times the resistance of the wire. The correction of R for the conductivity of the water is therefore insensible.

Platinum Wire No. 1. Diameter, 0·0505 cm. Water flow, 100 c.c. per second.

Approximate current.	$C^2 \times 25$.	R observed.	R calculated.	Difference.
0·6	10	0·13546	0·13547	+1
0·9	20	0·13546	0·13547	+1
1·3	40	0·13548	0·13548	±
1·8	80	0·13550	0·13550	±
2·5	160	0·13554	0·13554	±
3·6	320	0·13562	0·13562	±
5·1	640	0·13578	0·13578	±

The calculated values of R which are given in the table are from the expression

$$R = 0{\cdot}13546 + 0{\cdot}0000005\, C^2 \times 25.$$

This gives for α in the expression $R/R_0 = 1 + \alpha C^2$ the value $\alpha = 0{\cdot}000092$, which may be compared with the value found in the oil bath with "normal" stirring, which was $\alpha = 0{\cdot}0014$.

Hence by this arrangement, with a water flow of 100 c.c. per second, the effect is reduced to one-fifteenth of its former magnitude. If a platinum wire of 0·05 cm. diameter and 1 metre in length, having a resistance of about half an ohm, be used as a standard resistance for carrying currents up to 5 ampères, mounted as above described in a tube of about 1 cm. diameter, with a regulated flow of water of about 100 c.c. per second, it is therefore easy to apply the necessary correction, so as to obtain an accuracy of 1 in 50,000 on the resistance measured, and the error introduced by the conductivity of the tap water will be insensible.

In order to test the influence of the nature of the surface of the wire on the result, the same wire was coated with platinum black electrolytically, and afterwards submitted to a white heat in the flame of a Bunsen burner, whereby the platinum wire acquired a dull grey matt surface. The result was a small further reduction of α from 0·000092 to 0·000084.

In order to test the influence of water velocity on the result, the wire was submitted to a continuous constant current of a little over 5 ampères ($C^2 = 640/25$), and the bridge measurements were taken with the water flow varying from 100 c.c. per second to 1·37 c.c. per second. The results of this series of experiments are given in the subjoined table. The inflow temperature of the water was 21·3° C. The outflow temperature was

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sensibly the same as that of inflow for the first four or five measurements. For the last the outflow was about 0·6° higher than the inflow.

W. Water flow per second, in c.c.	R. Observed.	ΔR. Observed.	ΔR. Calculated.	Difference.
99·0	0·14026	12	12	±
93·0	0·14027	13	12	− 1
87·0	0·14028	14	13	− 1
74·5	0·14031	17	15	− 2
70·0	0·14035	21	16	− 5
55·0	0·14040	26	21	− 5
49·0	0·14044	30	23	− 7
40·0	0·14047	33	28	− 5
30·0	0·14056	42	36	− 6
26·0	0·14061	47	41	− 6
17·3	0·14079	65	58	− 7
12·3	0·14090	76	77	+ 1
8·2	0·14116	102	104	+ 2
4·7	0·14182	168	150	−18
1·37	0·14271	257	257	±

The calculated values of ΔR are obtained from the expression

$$R = 0{\cdot}14014 + \frac{0{\cdot}012}{W + 3{\cdot}3}.$$

This expression gives the value of R with infinite water flow as 0·14014. The "observed" values of ΔR are obtained by subtracting 0·14014 from the observed values of R.

The series of values of ΔR illustrates well the great importance of effective and regular stirring in securing a reliable correction for the effect. Even with the very small flow of 1·37 c.c. per second, the mean temperature of the cooling water is only 0·3° higher than in the first experiment, but the value of ΔR is 20 times as great, and the increase in the resistance is nearly 2 per cent.

With slow velocity of flow the turbulence ceases, and is replaced by a slow, gliding motion of the water along the wire. It is to this that the increased resistance is to be attributed, and not to the slight increase of temperature of the cooling water.

To determine the actual law of the effect as depending on the radius of the wire, four other wires were taken, drawn from the same material, and the resistances measured with varying currents and a uniform water flow of 100 c.c. per second. The results are given below; the resistance of each wire measured with an indefinitely small current being taken as unity. All these series of values satisfy the equation

$$R/R_0 = 1 + \alpha C^2.$$

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Experiment on Five Platinum Wires with uniform Water Flow of 100 c.c. per second.

$C^2 \times 25$	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
10	1·0000	1·0001	1·0003	1·0006	1·0014
20	1·0000	1·0001	1·0003	1·0011	1·0029
40	1·0001	—	1·0010	1·0023	1·0054
60	—	—	—	—	1·0085
80	1·0003	—	—	1·0045	1·0118
100	—	1·0008	1·0026	—	1·0143
150	—	—	1·0038	—	1·0212
160	1·0006	—	—	1·0090	—
225	—	1·0020	1·0062	1·0123	1·0313
300	—	—	1·0081	1·0169	—
320	1·0012	—	—	—	—
400	—	1·0036	1·0109	1·0224	—
450	—	—	1·0135	—	—
500	—	—	—	1·0272	—
640	1·0024	1·0058	1·0175	1·0345	—

The values of α, together with the diameters d of the wires, are given in the following table. The values for the diameters are each the mean of 10 measurements.

No. of wire.	d.	$\alpha \times 10^2$.	Log $(d \times 10^2)$.	Log $(\alpha \times 10^5)$.	$\alpha \times 10^2$ calculated.
1	0·0505	0·0092	0·703	0·962	0·0092
2	0·0352	0·0225	0·547	1·352	0·0225
3	0·0227	0·0675	0·356	1·826	0·0674
4	0·0169	0·140	0·228	2·146	0·141
5	0·0117	0·355	0·068	2·550	0·354

If in a diagram there are set out the values of $\log (d \times 10^2)$ as ordinates, and the values of $\log (\alpha \times 10^5)$ as abscissæ, the result is a straight line, which gives the relation

$$\log \alpha = \bar{8}\cdot719 - \tfrac{5}{2} \log d.$$

The values of α calculated from this expression are given in the last column of the table, and they correspond very accurately with the observed values. Hence, for a series of wires of similar material, similar surface, and with the same water flow, we have

$$\alpha = r^{-\frac{1}{2}} \times \text{a constant}.$$

If w be the resistance of the wire per unit of length and ρ the specific resistance, we have $w = \rho/\pi r^2$, and therefore

$$\alpha = r^{-\frac{1}{2}} w \times \text{a constant}.$$

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Furthermore, assuming that the whole effect is due to rise of temperature of the wire, and within the range for which the temperature-resistance curve may be taken as a straight line, we have

$$R/R_0 = 1+\alpha C^2, \quad R/R_0 = 1+\beta\theta,$$

where β is the ordinary temperature coefficient. Also by equation (1)

$$h = \frac{C^2}{\theta} \times \frac{R}{L} \times \frac{1}{2\pi J r};$$

and since $C^2/\theta = \beta/\alpha$ and $R/L = w$, we have

$$h = \beta w/2\pi J r\alpha, \quad \text{or} \quad h = \beta/2\pi J r^{\frac{1}{2}}.$$

Thus it follows for a series of wires of the same material that

$$h = r^{-\frac{1}{2}} \times \text{a constant.}$$

It thus appears that the "emissivity" of a round wire in contact with a liquid cooling agent is proportional to the inverse square root of the radius, when the other conditions of convective action of the cooling agent at the surface of the wire are kept constant.

The Properties of Colloidal Systems. III.—*The Osmotic Pressure of Electrolytically Dissociated Colloids.*

By W. M. Bayliss, F.R.S.

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An Experimental Investigation of Gibbs' Thermodynamical Theory of Interfacial Concentration in the Case of an Air-Water Interface.

By Prof. F. G. DONNAN, F.R.S., and J. T. BARKER, D.Sc.

(Received July 31,—Read November 9, 1911.)

(From the Muspratt Laboratory of Physical and Electro-Chemistry, University of Liverpool.)

1. *Introduction.*—Consider an aqueous solution of a substance S, the concentration being denoted by c. Let this solution be separated from another phase (oil, air, etc.), in which the concentration of the substance S is negligibly small. We may apply to this case Gibbs' fundamental equation*

$$\Gamma = -\frac{d\sigma}{d\mu},$$

where σ is interfacial tension, μ is chemical potential of S in the aqueous solution, Γ is mass of S per unit area of interface in *excess* of that corresponding to the uniform bulk-concentration of S in the solution.

It will be seen that Γ is, in fact, the amount of S per unit area of interface adsorbed or concentrated in the interfacial transition layer. If we are justified in applying the laws of dilute solutions, the above equation can be written

$$\Gamma = -\frac{c}{\mathrm{RT}}\frac{d\sigma}{dc},$$

where R is the constant of the simple gas equation and T is absolute thermodynamic temperature.

This equation is of fundamental importance in the study of the phenomena of the surface-accumulation of substances at the surfaces of separation of different phases. We may regard it as giving us a means of calculating the quantity Γ, the "capillary adsorption" at the interface. If $d\sigma/dc$ be negative, Γ will have a positive value, whilst if $d\sigma/dc$ be positive, Γ will be negative, that is to say, the concentration of S at the interface will be less than in the bulk of the solution.

In an experimental test of the validity of the equation, we must clearly deal with a freely mobile interface, in order that both Γ and $d\sigma/dc$ may be measured.

* Compare 'Scientific Papers,' vol. 1, p. 219, *et seq.*

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At the suggestion and under the direction of one of us, W. C. McC. Lewis* has investigated in this laboratory the case of a liquid-liquid interface, one liquid being an aqueous solution, the other a hydrocarbon oil. In the case of substances such as sodium glycocholate, sodium oleate, Congo red, and methyl orange, the directly measured value of Γ was found on an average to be about 60 times greater than the calculated value. It will be noticed that these are substances of high molecular weight, and of marked colloidal character in (concentrated) aqueous solution. The discrepancy is therefore most probably due to the occurrence of complex changes in the concentrated surface-layers, whereby colloidal aggregates, and possibly gelatinous or semi-gelatinous "skins," are formed. Smaller discrepancies were observed in the case of some simple inorganic salts, and in the case of caffein there was practical agreement between the observed and calculated values of Γ. Unfortunately, however, the adsorption was so small in these latter cases that the results partake more of a qualitative than a quantitative character. Recently,† the adsorption of aniline at the interface between an aqueous-alcoholic solvent and mercury has been measured by Lewis in a similar manner, and found to be in good agreement with the value calculated from the rate of variation of the interfacial tension with concentration. In these experiments, however, the effects measured were still not very great in comparison with the possible experimental error. It was decided therefore to investigate the phenomenon of capillary adsorption in a case where the effects would be as great and the conditions theoretically as simple as possible.

2. *Choice of Substances.*—On account of its high surface-tension, water was chosen as the solvent. In order to make the conditions, theoretically at least, as simple as possible, it was decided to investigate the adsorption (or surface-concentration) at the interface between water and air. It was necessary, therefore, to select a substance which should satisfy the following conditions:—

(1) It must be of simple and definite chemical composition, and give true aqueous solutions of simple and definite character.

(2) It must be, under the conditions of the experiments, practically non-volatile, and sufficiently soluble in water.

(3) It must in extremely dilute solution exert as powerful an effect as possible in lowering the tension of the air-water interface.

A search of the existing data showed that one of the saturated aliphatic carboxylic acids would be likely to satisfy all these conditions, and our choice finally fell on nonylic acid (pelargonic acid, $C_9H_{18}O_2$). The lower

* 'Phil. Mag.,' April, 1908, p. 499, and April, 1909, p. 466.

† 'Zeitschr. für physikal. Chemie,' 1910, vol. 73, p. 129.

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homologues of this series are too volatile, the higher not sufficiently soluble in water. We chose nonylic acid as sufficiently satisfying both the conditions specified in (2). The liquid acid was obtained from Kahlbaum, and its purity examined and tested with satisfactory results. Some preliminary measurements were made with solutions of sodium taurocholate, sodium glycocholate, and the corresponding free acids. The latter were found to be much more active than the salts. But since nonylic acid was found to be markedly more active than any of these substances, and possessed the further advantage of greater chemical simplicity, it was chosen as the best substance for our purpose.

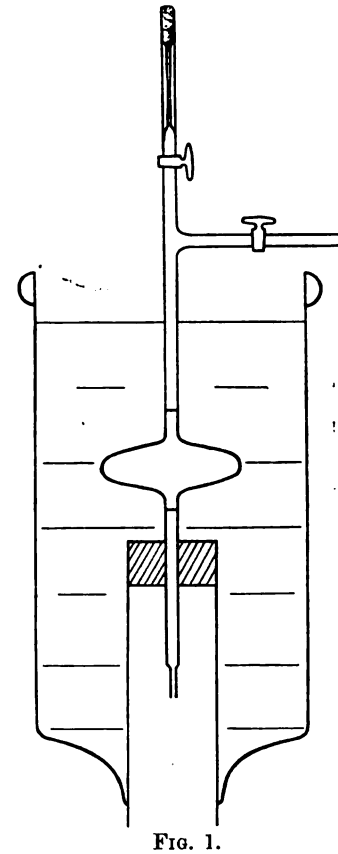

Fig. 1.

3. *Previous Investigations.*—The theory of surface-concentration at an air-water interface has been discussed by Lord Rayleigh,* especially in connection with the stability of foams. Lord Rayleigh's experiments on the surface-tension of a newly-formed aqueous soap solution and air interface have shown that an appreciable time is required for the formation of the more concentrated surface-layer. The existence of this surface-concentration in the case of an air and water interface has been demonstrated by the experiments of D. H. Hall,† J. von Zawidski,‡ F. B. Kenrick and Miss C. Benson,§ and S. R. Milner.‖ No satisfactory quantitative investigation of the phenomenon has, however, been carried out as yet.

4. *Analysis of Solutions and Determination of* $d\sigma/dc$.—For this purpose a dropping-pipette of the form shown in fig. 1 was employed.

The simple theory of the instrument¶ is that for a given size of opening the surface-tension is directly proportional to the weight of a drop, and hence, for very dilute solutions of practically equal density, inversely

* *Cf.*, for example, 'Proc. Roy. Inst.,' 1890—1892, vol. 13, p. 85.
† 'Proc. Roy. Dublin Soc.,' vol. 9 (N.S.), Part I, No. 10, p. 56.
‡ 'Zeitschr. für physikal. Chemie,' 1900, vol. 35, p. 77.
§ 'Journ. Phys. Chem.,' 1903, vol. 7, p. 532.
‖ 'Phil. Mag.' [6], 1907, vol. 13, p. 96.
¶ Lord Rayleigh, 'Phil. Mag.' [5], 1899, vol. 48, p. 321.

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proportional to the number of drops in a given volume. This holds strictly only for static equilibrium, the dynamic nature of the actual phenomenon necessitating a small correction.* This correction is unnecessary when we employ the drop number-concentration curve as a means of analysis. Even in the case of the determination of $d\sigma/dc$ from the (σ, c) curve we have employed only the simple (statical) theory, as we considered that the correction would not be large enough to sensibly affect our main conclusions.† It is necessary, however, that the rate of formation of the drops should be sufficiently small, as pointed out by Lord Rayleigh. In the case of dilute solutions of nonylic acid, where there is strong surface-concentration, the surface-tension of the freshly formed surface takes an appreciable time to arrive at its equilibrium value, and so the number of drops in a constant volume (the volume of the pipette) varies considerably with the speed of dropping. In order to obviate this source of error, which, if neglected, would have rendered our analytical results quite worthless, the speed of dropping was kept quite constant (or very nearly so) in all measurements (8·3 drops per minute). Under these conditions we found we could reproduce the drop-number of a solution of nonylic acid of given concentration to a fraction of a drop (in 300 to 500 drops). This procedure rendered the use of the dropping-pipette quite satisfactory for the purposes of analysis.

For the determination of relative surface-tensions it would, strictly speaking, have been necessary in the case of every solution to have determined the drop-number as a function of the speed of dropping, and to have extrapolated to zero speed. The (σ, c) curve determined by us for the constant speed of 8·3 drops per minute will not therefore quite coincide with the (σ, c) curve determined for an infinitely slow rate of dropping. The small error thus introduced in the values of $d\sigma/dc$ may be neglected in the present investigation, where we are concerned more with orders of magnitude than with high percentage accuracy.

The pipette shown in fig. 1 was water-jacketed to keep the contents at a constant temperature. The forming drop must be carefully shielded from draughts and vibration. The orifice consisted of a thin-walled cylindrical tube of about 2 mm. diameter sealed to the main stem. The external walls of the orifice must be kept dry and clean. The solution to be measured is sucked up into the pipette by means of the side tube, the tap of which is afterwards closed. The speed of outflow is regulated by fine capillary tubing

* Guye and Perrot, 'Archives des Sc. Phys.' (4th series), 1901, vol. 11, p. 225 ; 1903 vol. 15, p. 132. Kohlrausch, 'Ann. der Physik.,' vol. 20, p. 798 ; 1906, vol. 22, p. 191. Lohnstein, 'Ann. der Physik.,' vol. 20, pp. 237, 606 ; 1906, vol. 21, p. 1030.

† *Cf.* Lewis, 'Phil. Mag.,' April, 1908.

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attached to the top. Entrance of dust is prevented by suitable plugs of cotton wool.

The number of drops was automatically registered on the tape of a Morse recorder by allowing each drop to fall on a balanced vane of aluminium, the movement of which closed the relay circuit. Towards the end of the dropping the drops were counted by eye, in order to estimate to a fraction of a drop. The reliability of the automatic registration was frequently checked by direct counting.

The solutions of nonylic acid were made up by weight in distilled water, and were preserved in vessels of Jena glass which had been previously carefully cleaned and steamed out. Since sodium nonylate, like the sodium salts of the bile-acids, is much less active in lowering the tension of the air and water interface than the free acid, the drop-number of the solutions constitutes a very delicate test for their permanence in contact with glass. It was found that the weaker solutions remained unchanged for several days, whilst the stronger solutions showed a gradual fall in drop-number. Fresh solutions were therefore always used in these cases.

The following table gives the measurements of drop-number and surface-tension, as determined by us for solutions of nonylic acid (16·3° C.):—

Table I.

Concentration (c).	Drop-number.	Surface tension (σ).
grm. in 100 grm. solution.		dynes/cm.
0	324·8	72·91
0·000977	329·5	71·83
0·001260	330·7	71·65
0·002430	348·6	67·97
0·003290	364·5	65·01
0·005007	414·0	
0·005000	413·0	57·33
0·005005	413·0	
0·006810	449·0	52·77
0·007590	471·7	50·24
0·008060	482·7	49·09

The corresponding (σ, c) curve is shown in fig. 2. The most remarkable feature of this curve is the point of inflexion, which occurs at a concentration of about 0·004 per cent. This has also been observed by Forch,* who has determined the (σ, c) curve for nonylic acid and its homologues. It might be possible to ascribe this effect to the presence of small amounts of ammonia in the distilled water, since the ammonium salt would not be so active as the free acid. It seems more probable that the above form of

* 'Wied. Annalen,' 1899, vol. 68, p. 801.

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the (σ, c) curve really represents the true relation between σ and c. We have, however, directly measured Γ for several values of c lying between 0·0024 and 0·0080 per cent., in order to eliminate any doubt as to the true values of $d\sigma/dc$ corresponding to very small concentrations. For

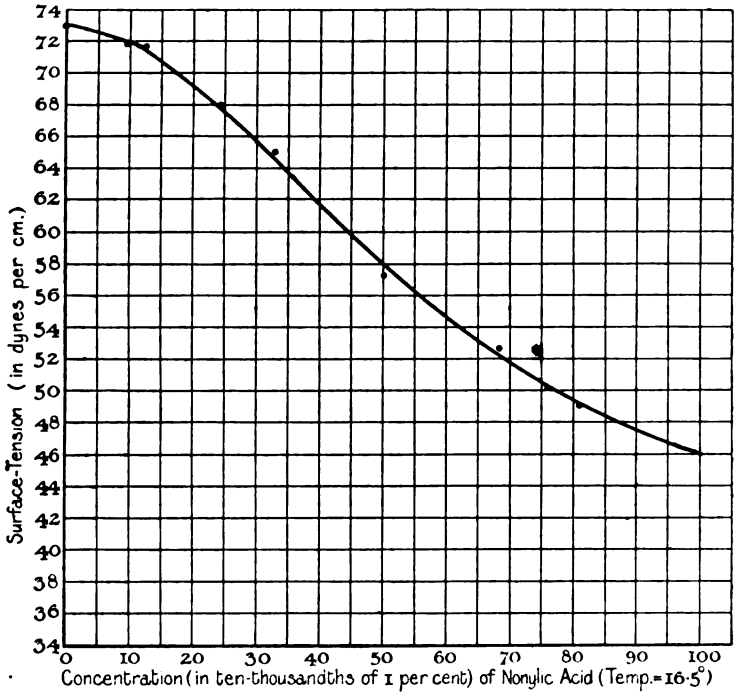

FIG. 2.

values of c higher than 0·0024 per cent., it seems probable from both Forch's curve and ours that the corresponding values of $d\sigma/dc$ would not be subject to the possible sources of error which might be effective in extremely dilute solutions, especially of acids.

5. *Experimental Determination of* Γ.—The principle of the method employed is as follows:—A large number of air-bubbles of uniform and known size are allowed to traverse a column of the solution. These bubbles carry on their surface a layer of more concentrated solution, due to the effect of the capillary adsorption at the air and solution interface. The bubbles are caused to collect (and break) in another vessel, so that the excess of solute thus returned to the bulk of the solution cannot find its way back to the column of solution referred to above. If we know the number and size of the bubbles and hence the total interface produced, and can determine with sufficient accuracy the total amount of solute removed as a result of the

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excess surface-concentration on each bubble, we shall clearly be able to calculate Γ directly.

Since we must work with very dilute solutions, in order to make Γ/c as large as possible $\left(\frac{\Gamma}{c} = -\frac{1}{RT}\frac{d\sigma}{dc}\right)$, and since the change of concentration produced by thousands of air-bubbles is, even in the case of very active substances, very small, an essential condition of success is the possession of a very delicate means of estimating these small differences of concentration of very dilute solutions. Ordinary chemical methods of analysis would quite fail us here. Fortunately the dropping-pipette itself provides us with the necessary weapon, owing to the rapid change of drop-number with concentration in the very region where the change of concentration has to be determined. It is only necessary therefore to determine the drop-number for the given solution before and after the bubbling, in order to be in a position to estimate the small decrease of concentration produced. A reference to Table I will serve to illustrate the degree of accuracy obtainable. For a 0·005 per cent. solution of nonylic acid a decrease in the drop-number of 1 drop corresponds approximately to a diminution of concentration of 0·000034 grm. per 100 grm. of solution. As we can estimate to half a drop with considerable certainty, it is possible to detect a change in concentration of 0·34 per cent. of its value in a solution containing only 0·005 grm. nonylic acid in 100 grm.

This degree of sensitiveness of the "capillary" method of analysis has made the measurements described in this paper possible.

The average drop difference observed amounted to about 4 drops, corresponding to a change of about 2·7 per cent. in the solution containing 0·005 grm. nonylic acid in 100 grm.

Putting the mean error of measurement at about one quarter of a drop, the above change of concentration could be estimated with an accuracy of about 6 per cent.

The chief difficulty encountered in the determination of Γ arose from the streaming of the liquid caused by the sweeping action of the rapidly moving bubbles. This streaming had the effect of mixing the liquid in all parts of the apparatus, and thus preventing the localisation of the decrease of concentration which we desired to measure. It was only after trying many forms of apparatus without success that we hit upon the simple device of breaking up the steady streaming motion of the liquid into a series of localised eddies, by means of a sort of inverted fractionating column.

The form of apparatus finally employed and the method of using it will be made clear by a reference to fig. 3.

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Air at constant pressure was delivered from the inverted bottle A. The arrangement for keeping the pressure constant will be readily understood from the figure. Since the air was delivered at constant pressure, the rate of bubbling was constant, and so the total number of air-bubbles could be estimated by determining the total time and the number of bubbles delivered during a short interval of time (five minutes). The constancy of the rate of bubbling was frequently checked during an experiment. The bubbles were formed at the jet B, which was made by sealing a piece of

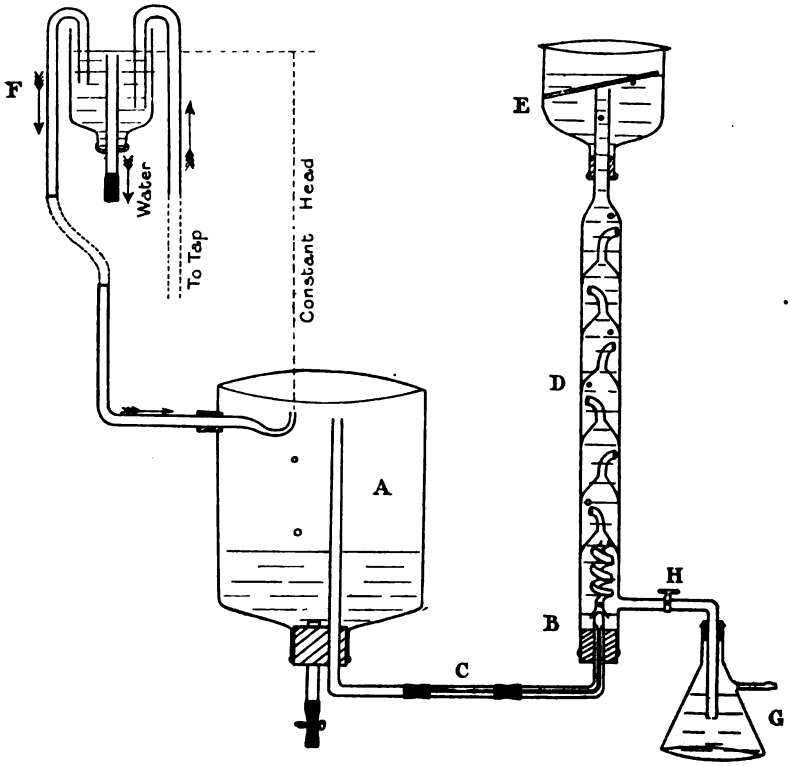

FIG. 3.

wider tubing to a piece of capillary tubing (or blowing a small elongated bulb at the end of the capillary tubing) and then heating and pulling this out to a fine conical point, the end of which was then snipped off. By means of this form of jet and the constricted capillary piece C, the bubbles formed regularly at the jet, "hanging" for a maximum period of five seconds before being dislodged.

After leaving the jet the bubbles had to traverse the glass spiral shown in the figure, taking about 20 seconds to do so. By means of these devices the change of concentration due to surface adsorption of the solute was localised

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as far as possible in the lowest compartment of the "fractionating" column D. The latter, as shown in the figure, was divided into a number of compartments by sealed-in inverted funnels, whose stems were alternately bent in opposite directions. That this arrangement had the desired effect, as explained above, was demonstrated by placing some $KMnO_4$ in the lowest compartment and bubbling air through for 20 hours. Even after this period the permanganate had not found its way into the upper compartments. The bubbles finally make their way into the wide vessel E, slide along the glass plate shown, and finally collect and coalesce at the surface of the liquid in E at places as far removed as possible from the point vertically above the exit tube of the fractionating column. In this way the excess of the solute produced by the breaking or coalescence of the bubbles at the surface of the liquid in E is prevented from finding its way back into the fractionating column. By analysing the total liquid contained in the first six compartments of the fractionator, we may therefore be sure of determining the total loss of solute due to the excess carried at the surfaces of the bubbles. In the earlier experiments the column D was water-jacketed to minimise mixing effects due to heat convection. Parallel experiments showed, however, that it was sufficient to keep the apparatus in a room of moderately constant temperature.

The volume of air delivered in an experiment was determined as follows:— When ready to start, A was completely emptied of water, connection was made with C by rubber pressure tubing, which was then compressed by a screw-clip, and water allowed to flow into A from the reservoir F until equilibrium was established. The experiment was then started. After completion, A was cut off from connection with C and F, and the contained water run out and measured. A was then closed to the air, water run in from F until pressure equilibrium was established with the same (constant) pressure-head as before, and then this water was run out and measured.

The difference of the two volumes of water gives the volume of air displaced from A under the constant pressure-head. This volume had to be corrected to that corresponding to the hydrostatic pressure at the jet. A further correction is required for the expansion of the bubbles during their ascent. In the actual adsorption experiments the liquid column above the jet measured 82 cm., corresponding to 60 mm. of mercury, and an expansion of the bubbles of about 8 per cent. of their volume. A correction for one-half of this was employed. No correction was applied for the capillary pressure in the bubbles, since, their average radius amounting to about 1 mm., the capillary pressure can be readily shown to amount to less than 0·2 per cent. of the total hydrostatic pressure at the level of the jet.

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From the volume of air thus determined and the number of air bubbles, the total adsorbing area is readily calculated.

The apparatus was filled and emptied as follows:—To fill it before an experiment, air pressure is applied through the side tube of the flask G, whereby the solution is driven from G into D and E. The tap H is then closed. During the filling air must be kept constantly bubbling from the jet, for, if this be not done, the solution gets into the capillary tubing and sets up a high capillary pressure. After the experiment is over the solution is syphoned off from E, and then the liquid in the six lower compartments of D removed by means of the side tube, measured, and analysed (by means of the dropping-pipette). The volume of solution so analysed was always 255 c.c.

The lower end of D was closed by a paraffined cork, through which the tube of the air-jet passed. It was found that this paraffined cork removed a little nonylic acid from a fresh solution, when the latter was allowed to stand in contact with the cork for 24 hours. A state of equilibrium was, however, attained, for the cork when so treated did not now affect another solution of nonylic acid of the same concentration. The precaution was, therefore, always taken of "saturating" the cork before an experiment was carried out. The validity of this procedure was amply demonstrated.

A further possible source of error was the vaporisation of the nonylic acid into the bubbles. It was therefore necessary to investigate by blank experiments whether any appreciable effect of this sort occurred. Air was bubbled continuously for 24 hours through solutions of nonylic acid contained in D, the top vessel E being removed. In this case the bubbles broke at the surface of the solution situated in the upper portion of the adsorption-vessel D. The solution was analysed before and after an experiment by means of the dropping-pipette.

The following results show that the vaporisation loss was extremely small:—

Strength of solution.	Drop-number before.	Drop-number after.
per cent.		
0·00243	349	348
0·005	410·4	410·1
0·00806	482	481

6. *Calculation of the Measured Adsorption.*—The method of calculating the adsorption from the experimental data will be made clear by the following example:—

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Data.—

Barometric pressure	728 mm.
Pressure-head in Reservoir A	125·4 cm. water = 92·3 mm. mercury.
„ at air jet	82 „ = 60·3 „
Volume of air driven over from A (at pressure in A)	90·5 c.c.
Temperature of experiment	15°—16°.
Number of bubbles per minute	24.
Duration of bubbling	20·6 hours.
Drop number of solution before experiment	482·7.
„ „ after „	479·3.
The total volume of air in the bubbles, calculated for half the height of the pressure-head in D	$90{\cdot}5 \times \frac{820{\cdot}3}{758{\cdot}2} = 97{\cdot}9$ c.c.
Total number of bubbles	$24 \times 60 \times 20{\cdot}6 = 29640$.
Hence the average diameter of a bubble	1·848 mm.,
and the total adsorbing area	3179 sq. cm.

With the drop-number and surface-tension curves given previously it can be calculated from the above data that the decrease of concentration of the nonylic acid amounted to 0·0001099 per cent., *i.e.*, 0·0001099 grm. per 100 c.c. Hence the total amount of nonylic acid removed by surface-concentration (adsorption) at the total air-liquid interface

$$= \frac{0{\cdot}0001099}{100} \times 255 = 0{\cdot}000280 \text{ grm.}$$

Whence follows $$\Gamma = \frac{0{\cdot}000280}{3179} = 0{\cdot}88 \times 10^{-7} \text{ grm./cm.}^2.$$

The experimental data are given in the following Tables.

The volumes given refer to the total volume of the air-bubbles, as corrected for the pressure-difference in the manner explained above. The change of concentration produced by the adsorption can be calculated in each case from the direct experimental data (determinations of drop-number before and after the experiment) by a reference to the curves given previously.

Table II.—0·00243-per-cent. Solution of Nonylic Acid.

Temp.	Volume of air.	Bubbles per minute.	Time.	Adsorbing area.	Drop-number.		$\Gamma \times 10^7$.
					Before expt.	After expt.	
° °	c.c.		hours.	cm.².			grm./cm.².
14·7—15·5	209	31·4	22·2	5920	348·6	344·7	0·93
14·0—15·7	272	41·4	19·3	7390	349·2	343·9	1·02
13·4—14·2	78	94·3	24·65	4574	346·1	343·2	0·90
							Mean... 0·95

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Table III.—0·00500-per-cent. Solution of Nonylic Acid.

Temp.	Volume of air.	Bubbles per minute.	Time.	Adsorbing area.	Drop-number.		$\Gamma \times 10^7$.
					Before expt.	After expt.	
° °	c.c.		hours.	cm.².			grm./cm.².
16·0—17·0	86·5	16·4	16·4	1904	408·3	404·9	1·71
14·0—15·0	105·5	5·0	41·3	2554	408·4	405·8	1·39
12·0—13·0	93·7	14·0	19·8	2550	409·5	406·5	1·25
13·5—14·3	106·1	22·6	19·2	3210	414·0	409·25	1·65
15·0	48·0	47·0	18·7	2387	414·7	411·0	1·71
13·8—14·8	47·0	47·6	19·3	2400	414·5	411·2	1·52
							Mean... 1·52

Table IV.—0·00759-per-cent. Solution of Nonylic Acid.

Temp.	Volume of air.	Bubbles per minute.	Time.	Adsorbing area.	Drop-number.		$\Gamma \times 10^7$.
					Before expt.	After expt.	
° °	c.c.		hours.	cm.².			grm./cm.².
13·9—14·4	186·0	13·5	21·7	4098	471·7	467·0	0·95
14·4—15·3	190·4	12·0	26·3	4262	466·25	460·0	1·23
							Mean... 1·09

Table V.—0·00806-per-cent. Solution of Nonylic Acid.

Temp.	Volume of air.	Bubbles per minute.	Time.	Adsorbing area.	Drop-number.		$\Gamma \times 10^7$.
					Before expt.	After expt.	
° °	c.c.		hours.	cm.².			grm./cm.².
13·0—14·0	121·0	20·0	18·5	3322	483·8	479·5	1·10
13·0—14·0	230·5	30·0	23·5	6373	483·8	477·6	0·81
14·0—16·0	97·9	24·0	20·6	3180	482·7	479·3	0·88
15·0—16·0	79·5	117·0	17·5	4440	482·1	477·5	0·87
							Mean... 0·915

It will be seen from the above figures that the values determined for each solution show a very satisfactory agreement amongst themselves, in spite of large variations in the speed of bubbling. It seems very probable, therefore, that the measured adsorptions represent the true equilibrium values. The mean results given in Tables II to V show a maximum adsorption occurring

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in the neighbourhood of 0·005-per-cent. concentration. The mean value of Γ, $1{\cdot}5 \times 10^{-7}$ grm. per square centimetre, obtained for the 0·005-per-cent. solution, deviates from the other mean values by an amount which appears to exceed the experimental error, but the latter values themselves lie pretty close together. More experimental work will be necessary before the existence of such a maximum is established beyond doubt.

7. *Calculation of* Γ *from the* (σ, c) *Curve.*—In calculating Γ from the equation $\Gamma = -\frac{c}{\mathrm{RT}} \cdot \frac{d\sigma}{dc}$, $\mathrm{R} = 2 \times 4{\cdot}2 \times 10^7$ ergs per gramme-molecular weight, if the gramme-molecular weight be taken as the unit of mass.

Since the molecular weight of nonylic acid is 158, we must put $\mathrm{R} = 2 \times 4{\cdot}2 \times 10^7 \div 158$ ergs per gramme, if we take the gramme as the unit of mass. In that case the equation will give Γ in terms of grammes per square centimetre.

This assumes that the nonylic acid is completely undissociated. Taking the electrolytic dissociation into account, we must write $\Gamma = -\frac{c}{i\mathrm{RT}} \frac{d\sigma}{dc}$, where i is van't Hoff's factor. Assuming complete electrolytic dissociation of the nonylic acid in the extremely dilute solutions employed, we have $i = 2$.

The values of $d\sigma/dc$ corresponding to the various values of c may be calculated from the (σ, c) curve obtained by the authors (see p. 560), or from Forch's curve.* The values of Γ calculated in this way, in ten millionths of a gramme per square centimetre, are shown in Table VI. For convenience of comparison, the experimentally determined values are included in the table.

Table VI.—Comparison of Observed and Calculated Values of Γ.

Concentration.	$\Gamma \times 10^7$ observed.	$\Gamma \times 10^7$ calculated—			
		From Forch's curve (18°)—		From our curve (16·5°)—	
		For $i = 1$.	For $i = 2$.	For $i = 1$.	For $i = 2$.
per cent.					
0·00243	0·95	0·58	0·29	0·55	0·26
0·00500	1·52	1·23	0·61	1·14	0·57
0·00759	1·09	1·58	0·79	1·26	0·63
0·00806	0·915	1·63	0·81		

The calculated values of Γ increase with the concentration, and do not show any maximum.

* Forch, *loc. cit.*

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It will be seen that the calculated and observed values of Γ agree as to order of magnitude. For $i = 2$ the agreement between the observed and calculated values is better at the higher concentrations. Considering the difficulty of measuring such small changes of concentration in the extremely dilute solutions employed, the agreement must be regarded as affording a verification of Gibbs' fundamental equation.

8. *The Adsorption of Saponine at an Air to Water Interface.*—An investigation of a similar kind to that carried out with nonylic acid was extended to the glucoside saponine. As is well known, this substance forms very stable foams and viscous films at the bounding surface of air-bubbles. This peculiar behaviour rendered an investigation of the surface adsorption in this case of considerable interest. Ordinary saponine is unfortunately not a very definite substance, its composition varying with the source of supply. The preparation used in the present work was Merck's "pure white" preparation. The mean molecular weight in aqueous solution was determined by freezing-point measurements, whereby moderately strong solutions were essential for obtaining an accurately measurable lowering of the freezing-point.

For solutions varying from 5 to 10 per cent., the mean value so found was 1260. This value has been employed in the subsequent calculation of the adsorption in very dilute solutions, although this procedure is open to some objection. We had, however, no means of determining the molecular weight in these very dilute solutions.

It was found necessary to work with fresh solutions, as the "drop-number" of a given solution, obtained with the same dropping-pipette, increases slowly with time, the increase becoming detectable with our apparatus in three to four days.

Furthermore, the drop-number was found to vary very considerably with the speed of dropping. This is probably due to the high molecular weight and consequent slow rate of diffusion causing a relatively considerable time to be required for the establishment of the surface-concentration at the fresh air and water surface.

Thus for the same volume of solution in the pipette the number of drops diminishes as the speed of dropping increases. As pointed out before in the case of nonylic acid (where a similar, though not so marked, effect occurs), this source of error has no effect on the use of the dropping-pipette as a method of analysis, provided one works under strictly constant conditions.

The following data were obtained with a constant total time of dropping (50 minutes). Temperature = 16·5°.

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Table VII.

Concentration of saponine.	Drop-number.	Surface-tension.
per cent.		dynes/cm.
0	324·6	72·91
0·0072	333·9	70·88
0·0143	345·9	68·42
0·0320	351·3	67·37
0·0433	353·8	66·89

The data of Table VII have been used for determining the change of concentration of the saponine solution employed in the experiments on adsorption. The corresponding surface-tensions are shown in Curve I of fig. 4. In order to ascertain the effect of variation of speed of dropping on the values of the surface-tension determined in this way, the following experiments were performed:—

Table VIII.

Drops per minute.	No. of drops.
Concentration = 0·00708 per cent.	
6·66	333·3
4·60	338·0
3·55	341·9
2·60	344·0
2·50	344·3
Concentration = 0·01413 per cent.	
6·90	346·5
4·77	349·2
3·66	351·5
2·59	353·0
Concentration = 0·032 per cent.	
7·03	351·3
4·43	354·6
2·62	357·7

Interpolating for the constant very slow speed of dropping of 2·6 drops per minute, the following results are obtained (temp. = 16·5°):—

Table IX.

Concentration of saponine (c).	Surface-tension (σ).
per cent.	dynes/cm.
0	72·91
0·00708	68·80
0·01413	67·04
0·032	66·16

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The data of Table IX are plotted on Curve II in fig. 4. It will be seen that in the initial part Curve II is considerably steeper than Curve I.

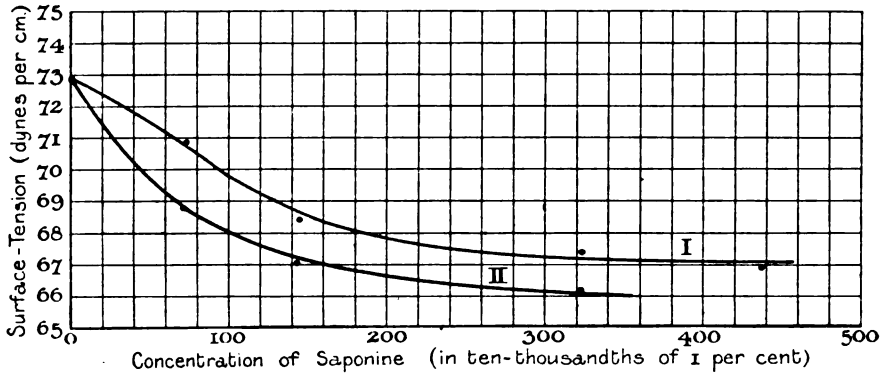

FIG. 4.

The adsorption was experimentally measured in the same manner as before, the results being given in the following table (temp. = 15°):—

Table X.—Concentration of Saponine = 0·0072 per cent.

Volume of air.	Bubbles per minute.	Time.	Adsorbing area.	Drop-number.		$\Gamma \times 10^7$.
				Before expt.	After expt.	
c.c.		hours.	cm.².			grms./cm.².
141·3	126	22·7	7290	336·7	334·0	5·2
205·1	147	24·8	10155	333·6	331·8	2·6
263·6	126	24·3	11313	334·4	332·0	3·1
						Mean ... 3·7

In order to calculate Γ in this case from the equation $\Gamma = -\frac{c}{iRT} \cdot \frac{d\sigma}{dc}$, we have $i = 1$ and $R = 8{\cdot}4 \times 10^7/1260$ ergs per gramme.

The results of this calculation and the experimentally determined adsorption for the same concentration (0·0072 per cent.) are as shown below :—

$\Gamma \times 10^7$ observed.	$\Gamma \times 10^7$ calculated.	
	$\frac{d\sigma}{dc}$ from Curve I.	$\frac{d\sigma}{dc}$ from Curve II.
3·6	1·36	1·60

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The observed value is about double the calculated value, but, considering the difficulties and uncertainties of the determinations, the agreement is not unsatisfactory. It would appear, therefore, that no irreversible "gelatinisation" occurs in the surface-layer of an aqueous saponine solution, at all events in the case of moderately fresh solutions. Possibly the "gelatinous skins" which may form on standing are due to secondary causes, or at all events to slow irreversible effects.

9. *Summary of Results.*—(1) The surface-tensions and surface-concentrations at an air to water interface have been experimentally determined in the cases of solutions of nonylic (pelargonic) acid and saponine.

(2) In the case of very dilute solutions the adsorption (surface-concentration) was found to be of the order of 1×10^{-7} grm. per square centimetre for nonylic acid, and of the order of 4×10^{-7} grm. per square centimetre for saponine. Working with solutions of sodium glycocholate, Congo red, and methyl orange, Lewis (*loc. cit.*) found the adsorption at an oil to water interface to amount to about 5×10^{-6} grm. per square centimetre.

(3) The values of the adsorption found for nonylic acid and saponine agree as to order of magnitude with the values calculated from Gibbs' equation. Considering the difficulties and possible errors of the experimental determinations, the agreement between the observed and calculated values may be regarded as a satisfactory verification of the validity of Gibbs' theory of surface-concentration for an air to water interface.

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On the Gaseous Condensable Compound, Explosive at Low Temperatures, produced from Carbon Disulphide Vapour by the Action of the Silent Electric Discharge.—II.

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In a former Note communicated to the Society* we described the change of a rapid current of carbon disulphide vapour at a low pressure, under the influence of the silent electric discharge or of the ultra-violet radiation associated with it, into sulphur and a gaseous substance, condensable and explosive near the temperature of liquid air, forming a brown solid, resembling the polymeric form of carbon monosulphide previously obtained by the chemical interaction of thiophosgene and nickel carbonyl.† This gaseous condensed substance will be called hereafter the ozoniser product.

The present paper contains an account of the further study of this change and of the product obtained.

A number of experiments were made to ascertain if the phenomena observed were in any way dependent on the presence of impurities in the carbon disulphide.

(1) Carbon disulphide was shaken first with concentrated sulphuric acid, then with mercury, and finally with lime, and was distilled, after which it was dried over pure phosphorus pentoxide. The whole of the apparatus was also dried by contact with pure phosphorus pentoxide for 14 days.

(2) Specimens of carbon disulphide were prepared from potassium trithiocarbonate and from potassium xanthate, dried and distilled, and were also submitted to the treatment described above before use.

(3) Purified carbon disulphide standing over phosphorus pentoxide at 15° C. was distilled into a bulb cooled in liquid air, and from this was passed into the ozoniser.

(4) Further, a quantity of charcoal was placed in the bulb containing the carbon disulphide, and the vapour was made to pass over a column of charcoal before it entered the ozoniser.

In all cases, however, when carbon disulphide distilling from the liquid

* 'Roy. Soc. Proc.,' A, vol. 83, p. 526. The investigation has been continued in the laboratories of Cambridge University and the Royal Institution, London.

† 'Roy. Soc. Proc.,' A, vol. 83, p. 408.

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kept at −78° C. into a charcoal condenser cooled to −185° C. was submitted to the action of the silent electric discharge, and the vapour together with any new product condensed in a **U**-tube placed in liquid air, a brown solid resulted, the formation of which was accompanied by a glow or a flash and usually by a detonation on removing the liquid air surrounding the **U**-tube. Hence it is clear that these phenomena are not caused by the presence of impurities in the carbon disulphide, and that the evolution of light and heat are definitely associated with the transformation of the condensed gaseous product into the brown solid. It will be seen later that the flash and the detonation are to some extent variable phenomena.

The apparatus used in the later experiments differed in some respects from that used originally. The bulb containing pure carbon disulphide, which was surrounded by a paste of solid carbon dioxide and ether, communicates through a tap with the annular space of the ozoniser. The ozoniser is connected by means of a 3-way tap with two quite similar **U**-tubes packed with finely-shredded cotton wool or asbestos that offer an equal resistance to the passage of the stream of vapour of carbon disulphide, and through a second 3-way tap to the charcoal condenser immersed in liquid air. When it was desired to observe the action of substances such as finely divided metals on the gases from the ozoniser these substances were either mixed with or deposited on asbestos, so that the deposit obtained when the gases were passed through it and subsequently condensed by liquid air could be compared with that obtained when the gases had passed over pure asbestos. Alternatively, either **U** could be left free of any filtering material, and the character and proportion of the material deposited compared.

In some of the experiments thick rubber tubing, previously soaked in molten paraffin, was used to make joints, so that the **U**-tubes could be removed and others substituted for them rapidly. In some cases powders and liquids were exposed to the action of the stream of vapour from the ozoniser.

Variation in Conditions of the Experiment.

In order to ascertain if the rate of production of the brown solid could be increased, experiments were made in which the vapour of carbon disulphide evolved from the liquid at different temperatures between −78° C. and 0° C. was allowed to pass through an apparatus in which an ordinary vacuum tube with flat platinum electrodes about 1 cm. in diameter replaced the ozoniser, and from this entered the wide tube condenser which replaced the **U**-tube used in other cases. Under these conditions the vapour was submitted to the action of the electric discharge passing between the

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platinum electrodes in the vacuum tube. The surface of the vacuum tube soon became coated with a whitish deposit of sulphur and later with the brown solid. The product condensed at the temperature of liquid air transformed into a brown solid with the evolution of light and heat as usual, and this occurred when the vapour had passed through the cotton-wool filter, but the phenomena were more striking when this was replaced by a plain tube, since under these conditions the quantity of material condensed in a given time is much increased.

Experiments were also made in which the ozoniser, which was of the simple tube form with external electrodes, was either cooled to $-80°$ C. or heated to 220° C., the other conditions being as usual. In both cases the brown solid was formed in the U-tube, but the quantity obtained was less than under the ordinary conditions of temperature.

In none of the experiments was the amount of brown solid obtained greater than in those in which the vapour from carbon disulphide at $-78°$ C. was passed through an ozoniser, and these conditions were therefore adopted for all subsequent experiments.

The determination of the ratio between the amounts of brown solid formed in the U-tube and of carbon disulphide passed through the ozoniser was found to be difficult owing to the almost invariable breaking of the U-tube during the transformation.

Several determinations were carried out successfully by collecting the carbon disulphide from the U-tube in a small capillary tube connected to the U-tube and measuring its volume and then determining the weight of solid left in the U-tube.

The ratio of the weight of the solid to that of the carbon disulphide varied from 1 to 10 to 1 to 50 in different experiments, and was found to depend on the form of the apparatus and the amount of solid surface which the ozoniser product passed over. Another very potent influence was found to be the deposit on the ozoniser surface. A clean ozoniser gave a much larger quantity of brown solid than an ozoniser that was coated with a deposit.

These ratios are lower than those given in the former paper; this is, however, partly due to the greater length of the tubes between the ozoniser and the U-tube and the introduction of a tap, which, as will be seen later, tend to reduce the amount of brown solid collected owing to a greater proportion of it being polymerised in the ozoniser and leading tubes. No difference in the behaviour of the ozoniser product has been traced to variations in the amount of carbon disulphide condensed with it.

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The Transformation of the Condensed Ozoniser Product into Non-Volatile Solid.

The solid deposited in the condenser at −185° C. is at first white, but soon acquires a brown colour, the darkest portion being that nearest the liquid air surface. On allowing the temperature to rise, the brown colour spreads rapidly, and this change is usually accompanied by a glow or flash and a detonation which may be violent enough to shatter the condenser The transformation may, however, take place quietly without an audible detonation or a visible flash, and, on the other hand, a detonation may take place while the condenser is still immersed in liquid air.

The interposition of a cotton-wool filter between the ozoniser and the condenser diminishes the intensity of the phenomena observed in the condenser to a very considerable extent, and at the same time increases the rate at which brown solid is deposited in the ozoniser and leading tubes. This is to be attributed chiefly to the fact that the rate at which the vapours pass through the apparatus is decreased by the filter. The active gaseous substance consequently becomes transformed to a greater extent into solid and deposited in the ozoniser, and on the large amount of surface of the cotton wool.

Quantitative experiment showed that the interposition of cotton-wool filters reduced the rate of flow of carbon disulphide to about one-fourth its former value, and the amount of brown solid to about one-fifteenth.

When the U-tube was replaced by a condenser of the test-tube form cooled to −210° C. by immersion in liquid air under exhaustion and the gases admitted, the solid deposit, which was formed on the bottom of the wide tube, was perfectly white. After 15 minutes, however, the deposit had acquired a brown colour, showing that even at −210° C. the transformation was taking place slowly. On allowing the temperature to rise to −185° C. the transformation took place more rapidly.

Examination for Presence of Solid Particles in the Gases from the Ozoniser.

An arrangement of a litre bulb with a U-tube on either side was sealed between the ozoniser and the charcoal condenser. An arc lamp was arranged to project a beam of light through this relatively large space filled with the transforming material from the ozoniser. The glow in the ozoniser was screened off, and thus any solid particles in the bulb would be made evident by continued illumination of the beam through the bulb. The conducted glow of the transformer caused an appearance like a faint brush discharge across the bulb, but this of course was quite lost when the arc lamp was on.

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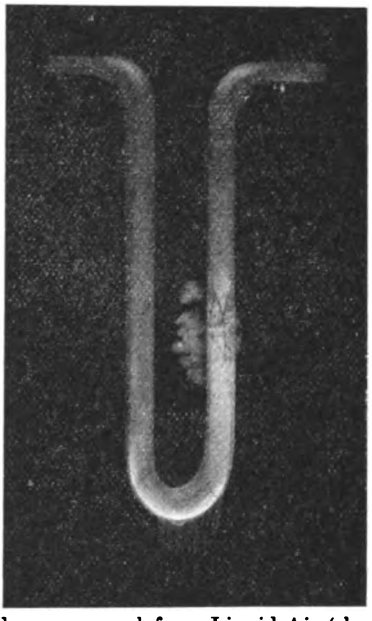
No visibility of the arc lamp beam within the bulb was seen, whether it was arranged converging to a focus or was parallel. The beam was of course easily visible by the motes in the air right up to the bulb and beyond it, but within was absolute darkness. Several good patches of transforming material were taken on the bulb by local condensation with a cotton-wool plug full of liquid air. In 35 seconds after turning off the discharge in the ozoniser only white carbon disulphide was thus condensed, all the transforming material having gone. A five minutes' deposit taken in the second U-tube beyond the litre bulb gave the usual detonating transformation, and shattered the U-tube. A similar deposit taken in the first



Exploding Deposit in U-tube on removal from Liquid Air (shaded portion due to flash of light).

U-tube produced, however, a distinctly more violent effect, and 2 or 3 inches of the tubes were completely shattered. No cotton-wool plug was used between the ozoniser and the bulb in the above experiment. Similar results as to non-visibility of the beam within the bulb were obtained when a cotton-wool plug was used; but, as usual, the deposits now gave less violent transformations. These observations indicate that the transformation of the gas into the brown solid only takes place in contact with solid surfaces.

The detonation of carbon disulphide with the production of carbon and sulphur could, theoretically, produce a temperature above 2000° C., and if

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the transforming ozoniser product is comparably endothermic, then a similar rise of temperature might occur if it could decompose in the same manner.

We have proved that the temperature produced during the transformation is high by taking a photograph of the U-tube by its own detonating flash by means of a camera placed 18 inches from the tube in a dark room. The figure is a photograph of a detonating deposit in a U-tube in which the cracks in the fractured tube are plainly seen. A flame is seen bursting through one such crack, and the light extends for a considerable distance through the tube.

Before allowing the deposit to flash by the removal of the liquid air, in some experiments the U-tube was filled with dry nitrogen at atmospheric pressure, through a three-way tap on the charcoal bulb. The right-hand limb of the U-tube contained copper wire gauze to cool the entering nitrogen and thereby prevent any undue heating of the deposit.

Two seven-minute deposits were successfully flashed after filling in the nitrogen. In both cases a violent detonation resulted, and the tube was shattered. The photographic plates showed good pictures of each flash, which was seen to be localised and not so intense, due no doubt to the relatively large pressure of nitrogen in the U-tube compared with previous experiments in which no inert gas was present.

Photographs of the Spectrum of the Flash.

The arrangement used to secure a photograph of the spectrum of the flashes consisted of a German silver U-tube with a quartz window at the top of one limb. The window was a conical plug about 2 cm. long and less than 1 cm. in diameter, ground into a brass fitting brazed on to a vertical extension of one limb of the U-tube. The fitting was also provided with a screwed nut to hold the plug in against the shock of the detonation. The flash occurring in the tube was, by means of a quartz prism, projected through the quartz plug and reflected on to the slit of a Hilger quartz spectrograph. The prism and U-tube were arranged quite close to the slit, which was $\frac{1}{2}$ mm. wide. Several flashes could thus be taken without the delay caused by the breaking of glass U-tubes, or the use of a quartz U-tube. After a few flashes the underside of the quartz window became obscured by a brown film. It was, however, a simple matter to remove this plug and replace it after cleaning. It should be remarked that the stopcocks on either side of the metallic U-tube were usually closed before taking the flash, although several times this occurred prematurely owing to the conduction of heat to the deposit through the metal tube.

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About seven flashes from deposits of 15 minutes' periods were necessary to get a good image of the spectrum.

The sulphur bands, wave-lengths between 384 and 392, and the cyanogen line 3885 were present. The principal hydrocarbon bands were plainly visible, of which that at 436—443 was the strongest in the whole spectrum. A strong band at 635—665 and scattered bands from 248 to 362 were present also, and fainter bands from 540 to 605.

The solid product got after the flashes taken in the metal tube was found to be practically a mixture of carbon and sulphur due to the high temperature of the flash, as the character of the spectrum tends to show.

Tests for Electric Effect in the Transformation of the Condensed Ozoniser Product.

A receiver was constructed for condensing the ozoniser product on a hollow thin platinum cylinder at liquid air temperature, and the deposit was then allowed to transform, the cylinder being electrically connected to a charged electroscope.

When connected to the ozoniser and exhausted such a condenser did not induce any electroscopic leak.

On cooling the platinum cylinder end of the tube in liquid air no charge was communicated to the electroscope. If the liquid air was removed and the cold tube touched or slightly rubbed, a charge was at once given to the electroscope. Such a charge remained almost without diminution.

The effect of the transformation of the deposit was tried by collecting a deposit for five minutes on the platinum cylinder, by cooling the end of the tube in which it was placed to liquid air temperature while the discharge passed in the ozoniser in the ordinary way. The stopcocks both on the ozoniser and the charcoal were then closed, the electroscope charged, and the liquid air removed to allow the deposit to transform as usual.

If only a feeble flash from a small short-time deposit was obtained, no effect was observed on the electroscope. If, however, a good bright flash was produced, then the leaves of the electroscope fell together a distance of not more than 2 mm., even with the most intense flash. In ordinary cases the charge remained practically unaltered, and the same effect was repeatedly observed whether the electroscope was charged positively or negatively. If the electroscope was uncharged at the time of the flash, no charge occurred on the transformation of the deposit.

Attempts to Concentrate the New Gas.

It was found that the gas was completely condensed in a **U**-tube at $-185°$ C. but that a similar **U**-tube, with a cotton-wool plug in the limb

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remote from the ozoniser, cooled to −120° C. by immersion in solid carbon dioxide under reduced pressure, allowed some of the gas to pass through it and to be condensed in a second **U**-tube at −185° C. The carbon disulphide used had been distilled at a low temperature under reduced pressure and kept over charcoal and anhydrous baryta.

The resistance of the cotton-wool plugs was estimated by cooling the carbon disulphide bulb to −78° C. and cooling the second **U**-tube in liquid air. In five minutes a deposit 15 to 20 mm. in length was formed in this **U**-tube.

The first **U**-tube was now cooled to between −115° and −120° C. A slightly less dense deposit was obtained in the second **U**-tube in five minutes.

The two **U**-tubes being thus at −120° and −185° C. respectively, the discharge was started in the ozoniser. In five minutes no coloured deposit could be seen in the **U**-tube in liquid air, but later the deposit became coloured, and in 20 minutes a distinct brown ring was observed at a point 3 mm. above the liquid air surface.

Where the gases entered the first limb of the **U**-tube at −120° C. a white crystalline deposit was observed; this did not melt until the temperature had risen almost to 0° C., when it distilled back into the bulb containing carbon disulphide.

This indicates that the ozoniser product contains two substances, and shows that the substance which gives rise to the brown solid is not condensed by cooling to −120° C., but passes on and is slowly transformed into the brown solid in the **U**-tube at −185° C.

Action of Coconut Charcoal and Rubber.

The vapours were passed over 0·5 to 1 grm. of coconut charcoal placed between the ozoniser and the **U**-tube at −185° C. When no discharge was passing through the ozoniser a white deposit of carbon disulphide began to appear in the **U**-tube after 10 minutes. When a discharge was passing through the ozoniser a similar white deposit appeared in 10 minutes, which deposit remained colourless and evaporated completely when the temperature was allowed to rise.

The ozoniser product is therefore absorbed, destroyed, or caused to polymerise by charcoal. The same result was obtained when the charcoal was cooled to −78° C. or heated to 250° C.

The vapours were now passed over 1 grm. of finely shredded rubber in order to absorb some of the carbon disulphide. The brown solid was formed as usual, but the amount of carbon disulphide deposited with it was

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distinctly less. It therefore appears that a partial separation of the transforming ozoniser product from the disulphide has been effected.

A complete separation of the two substances seems to be for the present out of the question on account of the rapidity with which the ozoniser product polymerises in the solid state at low temperatures.

Collection and Analysis of the Solid Product.

A quantity of the brown solid was now collected in order to ascertain its composition and properties after the removal of any free sulphur. For this purpose the cotton-wool filter was removed and the U-tube condenser replaced by one having the shape of a large test-tube. In this way the deposit was formed over a large area of the wide tube, and the risk of fracture during the transformation diminished. Experiments were carried on for from six to ten hours, and at intervals of about 30 minutes the liquid air was removed and the deposit allowed slowly to transform. At the end of the operations the condenser was broken, and the brown solid removed. Owing to the frequency with which glass U-tubes were shattered by the detonation accompanying the transformation of the deposit they had to be abandoned, as it was found extremely difficult to collect appreciable quantities of the deposit: all the more so as the substance adhered to the glass.

Finally, in one experiment, lasting six hours, at the end of which the glass condenser was intact, enough material (0·1127 grm.) was obtained to allow of the estimation of sulphur in it,

which gave S = 71·8 per cent.,

CS requires S = 72·7 per cent.

Further, the ratio C : S was determined in another specimen collected from number of experiments in which the condenser had been cracked and shattered. This specimen was probably contaminated with minute fragments of glass and also contained moisture. The material gave on analysis:—

S = 61·0 per cent., C = 24·6 per cent., and ratio C : S = 1 : 0·854,

or, allowing for the 5 per cent. of water present as impurity,

C : S = 1 : 0·93.

The substance produced in the manner described has the composition of carbon monosulphide, and it seems justifiable to conclude that, under the influence of the silent electric discharge, carbon disulphide has, like carbon dioxide under similar conditions, been dissociated, in this case into sulphur and gaseous carbon monosulphide, and that the latter can polymerise with the evolution of a considerable amount of energy to form a brown solid even

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at the temperature of liquid air. It is the remarkable instability of the solid or liquid gas at low temperatures that is so characteristic and renders the physical and chemical examination so difficult.

Material Deposited in the Ozoniser.

In all experiments the ozoniser gradually became covered with a brown deposit; the rate at which this accumulated was much increased when the rate of flow of vapour through the apparatus was diminished by the introduction of a cotton-wool or asbestos filter.

In order to remove sulphur as completely as possible from the deposit, about half a gramme of it was heated to 380 to 400° C. for some hours in a vacuum maintained by charcoal cooled in liquid air. The residue gave with sulphuric acid the brown-purple colour characteristic of the polymeric form of carbon monosulphide, and an estimation of the amount of sulphur gave 69·6 per cent., while CS requires 72·7 per cent.

Hence it would appear that a mixture of free sulphur and a polymeride of carbon monosulphide is deposited in the ozoniser.

Losanitsch* observed the formation of a brown deposit when carbon disulphide was exposed to the action of the silent electric discharge, and concluded from its composition that it was a polymeride of carbon disulphide, whereas it was probably a mixture of sulphur and the polymeride of carbon monosulphide.

Chemical Reactions of the Ozoniser Product.

The action of a number of substances on the ozoniser product was studied by placing the substances to be examined; either mixed with or deposited on asbestos in a U-tube, and allowing the vapours to pass over them.

In this way it was found that the passage of the ozoniser product was prevented by finely divided platinum, nickel, or silver.

In the last-mentioned case only could any change in the appearance of the metal be detected; white precipitated silver gradually acquired a bronze colour, and ceased to prevent the passage of the ozoniser product. When the silver was subsequently heated with concentrated sulphuric acid, the characteristic colour given by polymeric carbon monosulphide was obtained. Finely divided nickel was found to be particularly active, since 0·05 grm. was still able to prevent the passage of the ozoniser product completely after it had been in use for 15 hours, and its weight had increased 0·048 grm. Treatment of the nickel with concentrated sulphuric acid or

* 'Ber.,' 1907, vol. 40, p. 4656.

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with nitric acid failed to show the presence of polymerised carbon monosulphide, although both carbon and sulphur were present. The same applies to platinum and carbon, hence these substances seem to be capable of causing decomposition of the ozoniser product.

Ferric oxide (not ignited), yellow mercuric oxide, and silver oxide were found to react with the ozoniser product to form sulphides of the metals; ferric oxide is much more efficient than the other two oxides.

In the case of ferric oxide the reaction was investigated more fully by collecting the gaseous products in a small tube containing 0·2 grm. charcoal placed in liquid air, and then extracting and examining the gas, which was found to consist of carbon dioxide and carbon monoxide.

Solid caustic potash, silver nitrate, lead acetate, and sodium peroxide seemed to have little or no action on the ozoniser product, while barium peroxide reacted with it, forming barium sulphide.

When the vapours were passed over the surface of nitric acid, the ozoniser product was entirely destroyed.

The most striking reaction we have observed is that which takes place with concentrated sulphuric acid. After some experiments had shown that, as used, the vapour of carbon disulphide was not attacked by sulphuric acid, the ozoniser product was allowed to pass over the surface of sulphuric acid placed in a wide **U**-tube. The sulphuric acid rapidly acquired a yellow colour, changing gradually into deep orange-red, then became turbid, and deposited a yellow solid; brisk effervescence occurred during the whole time, and even after several hours none of the ozoniser product escaped the action of the acid. The yellow solid which separated from the sulphuric acid was found to be sulphur. In order to examine the gaseous products, the reaction was carried out in an apparatus with no rubber connections, and the gases produced were collected in a small charcoal condenser placed in liquid air, from which they were subsequently expelled and examined.

One experiment, which lasted three hours, gave: 10 c.c. of gas, of which 5 c.c. were sulphur dioxide; 2·2 c.c. carbon dioxide; 2·2 c.c. carbon monoxide; and the remainder nitrogen.

Effect of Mixing Carbon Disulphide Vapour with that of Other Substances.

In order to ascertain whether the presence of other substances in the ozoniser would influence the result of the action of the silent electric discharge on carbon disulphide, or in any way modify the phenomena accompanying the transformation of the product, some experiments were made in which hydrogen, nitrogen, ethyl ether, methyl iodide, or chloroform was passed through the ozoniser, together with the carbon disulphide.

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The introduction of hydrogen or nitrogen was effected by allowing the pure dry gas to leak slowly through a capillary tube dipping in the carbon disulphide. Ether was mixed with the liquid carbon disulphide in the proportion of two to one by volume, while methyl iodide or chloroform were volatilised from separate bulbs fitted with taps connected to the apparatus. The methyl iodide bulb was kept at −78° C., and the chloroform one at −69° C., so that the vapour in each case was used at approximately the same vapour-pressure as that of the carbon disulphide.

In each of the five cases mentioned above, the usual phenomena were observed. In the case of the gases hydrogen and nitrogen this is only true for small leaks, since larger quantities of gas reduce the vacuum, and so prevent the passage of a rapid stream of vapour through the ozoniser.

Methyl iodide and chloroform were themselves decomposed on passing through the apparatus, with the production of iodine and chlorine respectively, but these products did not interfere with the formation of the brown solid, which was accompanied by the usual flash and detonation.

Other Sulphur Compounds Examined.

A number of other sulphur compounds have been submitted to a treatment similar to that which results in the decomposition of carbon disulphide; a rapid stream of vapour at a pressure of about 1 mm. or more was exposed to the action of the silent electric discharge in an ozoniser, and also exposed to the electric discharge between platinum electrodes in a vacuum tube and the products collected in a condenser at −185° C.

The following substances have been examined in this way:—Thiophosgene, diethylsulphocarbonate, diethyldithiocarbonate, diethyltrithiocarbonate, and thiophene, but in no case has the production of carbon monosulphide been observed.

Properties of the Brown Solid Produced by the Electric Discharge Compared with those of the Polymeric Form of Carbon Monosulphide Previously Described.

The properties of the brown solid produced from carbon disulphide as described above, called A for brevity, which has been shown to have the composition of carbon monosulphide, have been compared with those of the polymeric form of carbon monosulphide, called B, obtained from the interaction of thiophosgene and nickel carbonyl.

The density of A is about 1·88 and is appreciably greater than that of B, which is about 1·6, or 1·83 when compressed.

B dissolves in concentrated sulphuric acid in the cold to produce an intensely brown purple coloured solution, while A only dissolves in the same substance above 100° C., and produces a similar coloured solution.

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Both A and B dissolve in concentrated nitric acid, forming red solutions.

B dissolves readily in alcoholic solutions of caustic soda and sodium hydrosulphide, forming black solutions, whereas most specimens of A dissolve in these solvents only to a slight extent after long boiling.

B is slightly soluble in certain organic solvents such as carbon disulphide, nitrobenzene, and ethylene dibromide, whereas A is practically insoluble in such solvents.

The action of heat on both substances is practically the same; at a dull red heat, in absence of air, carbon disulphide and carbon are produced from each. Actually this change takes place slowly at the boiling point of sulphur, and at this temperature B decomposes more rapidly than A, but the difference is slight. Since we find that a mixture of carbon and sulphur also slowly yields carbon disulphide at the boiling point of sulphur, the above observation does not serve as a distinction between a compound of carbon and sulphur and a mixture of these elements.

Both A and B when mixed with sulphur and heated to 440° slowly yield carbon disulphide, and the amount obtained in the same time is approximately twice as great as when either is heated alone. The observation recorded in the "Note on Carbon Monosulphide"* was erroneous, and the behaviour of the polymeric form of carbon monosulphide prepared from the interaction of thiophosgene and nickel carbonyl agrees in this respect with that of the substance obtained by Sidot by the action of light on carbon disulphide.

The above comparison of properties indicates that the difference between the brown substance obtained by the action of the electric discharge on carbon disulphide vapour and the polymeric form of carbon monosulphide obtained from thiophosgene may be merely in the degree of polymerisation. Such differences seem to exist between the products of the action of light on carbon disulphide at −80° C. and at the ordinary temperature, and between different specimens of the product from thiophosgene depending on the temperature to which they have been heated in drying, since in these cases different specimens show differences in density and in solubility.

In the experiments on the action of heat on the substance produced by the electric discharge, in which this was heated alone in a vacuum maintained by charcoal cooled in liquid air, it was found that a small quantity of molecular sulphur sublimed on the cooler parts of the tube. This was never observed when the substance obtained from the thiophosgene was similarly treated. It is difficult to be quite certain that the substance did not contain small quantities of sulphur carried over from the ozoniser, but

* *Loc. cit.*, p. 413.

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this suggests that the brown solid obtained from the transformation of the condensed gas consists partly of a mixture of carbon and sulphur resulting from the decomposition of a portion of the substance at the high temperature to which it is subjected during the transformation.

In those cases in which the transformation of the condensed product into the brown solid was accompanied by a detonation which shattered the condenser it was found that a thin deposit of fine soot partly covered the **U**-tube; this observation also points to the decomposition of a portion of the substance, or of some of the carbon disulphide mixed with it, under the influence of the high temperature produced. Further, in the experiments in which a metallic **U**-tube was used the material collected did not give the colour tests for polymeric carbon monosulphide; therefore in this case the decomposition of the carbon monosulphide appears to have been practically complete.

Other Methods of Producing Polymeric Forms of Carbon Monosulphide.

It has been shown above that the ozoniser product polymerises under certain conditions with explosive violence to produce a substance resembling the polymeric form of carbon monosulphide which was produced by the interaction of thiophosgene and nickel carbonyl, previously described. A polymeric form of carbon monosulphide was also obtained by Sidot,* and this method of production has been further studied.

Pure carbon disulphide at 15° C. or −78° C. is slowly changed on exposure to light to a yellowish-brown solid and sulphur. The solid is deposited on the walls of the containing vessel and soon cuts off the light and prevents further action, hence only very small quantities of the product can be obtained in this way, but it was found to give the brown-purple colour with sulphuric acid. The colour and density of the products obtained under different conditions varied to a greater extent than those of the products obtained from thiophosgene, but all seem to be carbon monosulphide polymerised to different degrees.

In order to obtain a quantity of the product of the action of light on carbon disulphide we made use of the fact that the product is soluble in sulphuric acid. Flasks containg 100 c.c. of pure carbon disulphide and 200 c.c. of concentrated sulphuric acid were exhausted, sealed, and exposed to sunlight for three months, during which time they were shaken vigorously at frequent intervals.

The action of light was rapid at first and the product was removed by the sulphuric acid which became highly coloured and opaque, but finally the

* 'Comptes Rendus,' 1872, vol. 74, p. 179; 1875, vol. 81, p. 32.

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action became extremely slow, probably owing to the absorption of the light by the solution of sulphur in carbon disulphide. On opening the flasks the odour of sulphur dioxide was observed. The sulphuric acid was slowly poured into water, when a dark flocculent precipitate separated, together with some sulphur.

The precipitate was filtered, washed, and dried at 150° C. in a vacuum. In one such experiment the product weighed 0·201 grm., and was found to contain 81·3 per cent. of sulphur.

In another experiment the product was heated for three hours to 360° C. in a carbon liquid air vacuum and was then found to contain 74·1 per cent. of sulphur. CS requires 72·7 per cent. This product exhibited all the characteristic properties of the polymeric form of carbon monosulphide.

The interaction of the polymeric form of thiophosgene $(CSCl_2)_x$ and nickel carbonyl has also been studied. The reaction takes place slowly in the cold and rapidly at 100° C., with the production of carbon monoxide, nickel chloride, and a polymeric form of carbon monosulphide having all the properties of the product obtained from thiophosgene, or by the action of light on carbon disulphide.

Specific Heat and Heat of Combustion of Polymeric Carbon Monosulphide.

Owing to an oversight, the values obtained for the specific heat and heat of combustion of the polymeride of carbon monosulphide obtained from thiophosgene were omitted from the note describing this substance, and are therefore included here.

The specific heat of this polymeric form of carbon monosulphide was determined between +15° C. and −185° C. by means of the liquid air calorimeter. A specimen of the substance compressed into a block was used and two determinations gave the values 0·128 and 0·126: the mean of these gives 5·59 as the molecular heat of carbon monosulphide. The atomic heat of carbon for the same range of temperature is 1·236 and that of sulphur is 4·32, the sum of these, 5·556, is very nearly the same as the value found for the molecular heat of the compound. The specific heat and latent heat of fusion combined, of carbon disulphide, for the same range of temperature is 0·222, or, as we should expect, much higher than that of the $(CS)_x$.

Two determinations of the heat of combustion of this carbon monosulphide were made in a bomb calorimeter and the values 179,700 and 176,400 calories were obtained for the reaction $[(CS)_x\ 2O_2]$. Taking the mean of these, the value for the heat of formation of $(CS)_x$ is found to be −10,000 calories, which is approximately half that of carbon disulphide.

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Production of Solid Oxygen by the Evaporation of the Liquid.

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It seems strange that while liquid hydrogen or nitrogen can easily be changed into the solid condition by evaporating the respective liquids under exhaustion, yet the ordinary air pumps fail to effect the transition of state in the case of liquid oxygen. This is due to the small vapour pressure of solid oxygen at its melting point, as compared with hydrogen or nitrogen under similar conditions; together with the greater need of very perfect heat isolation in the arrangement of the experiment. By means of the use of charcoal as a gaseous condensing agent at low temperatures, combined with the employment of proper vacuum vessels, the change from the liquid into the solid can be easily effected.* Pure liquid oxygen, contained in a properly isolated vessel, subjected to the exhaust produced by a quantity of charcoal kept at about the temperature of boiling oxygen, has its pressure lowered sufficiently to produce solidification to a transparent jelly. The pressure at which solidification takes place was determined by connecting a McLeod gauge to the vessel containing the solid oxygen.

About 75 grm. of good coconut charcoal is necessary to produce and maintain the necessary conditions of exhaust. From 5 to 10 c.c. of liquid oxygen were employed, previously exhausted by an air pump. The oxygen exhibits considerable supercooling, and a pressure of less than half the melting pressure can usually be maintained on the liquid without producing solidification. These experiments indicate that the melting point pressure is between 1·115 and 1·125 mm.

Fig. 1 shows the arrangement of the apparatus. Fig. 2 shows a modification in which the oxygen is contained in a bulb immersed in the solid oxygen produced by the charcoal exhaust.

In fig. 1, A is a silvered vacuum-jacketed tube, with a slit not coated, containing the oxygen to be exhausted. This is further isolated by a larger vacuum tube B, also silvered, and with a slit as above, which contains liquid air under an exhaust of less than 20 mm. A is sealed by the tube E on to a T-piece, whose limbs connect (1) through a constricted portion to bulbs

* This was publicly shown at a Friday evening Address given at the Royal Institution on January 20, 1911.

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containing permanganate of potash crystals and phosphoric anhydride respectively, (2) to a three-way cock C, sealed on to the arms of which are (*a*) the bulb D containing 75 grm. of coconut charcoal, (*b*) a T-piece connecting to the mercury-pump stopcock and the McLeod gauge respectively.

By starting the mercury pump, and arranging the cock C in position ⊖, so that I, II, and III are all connected, the whole apparatus, including the permanganate crystals and phosphoric anhydride bulbs, could be exhausted, the charcoal being well heated, and the exhaust obtained read on the gauge.

Such a large mass of heated charcoal prevents the exhaust for practical purposes being brought below 0·01 mm.

When the pressure is reduced to this order, the cock C is turned to the

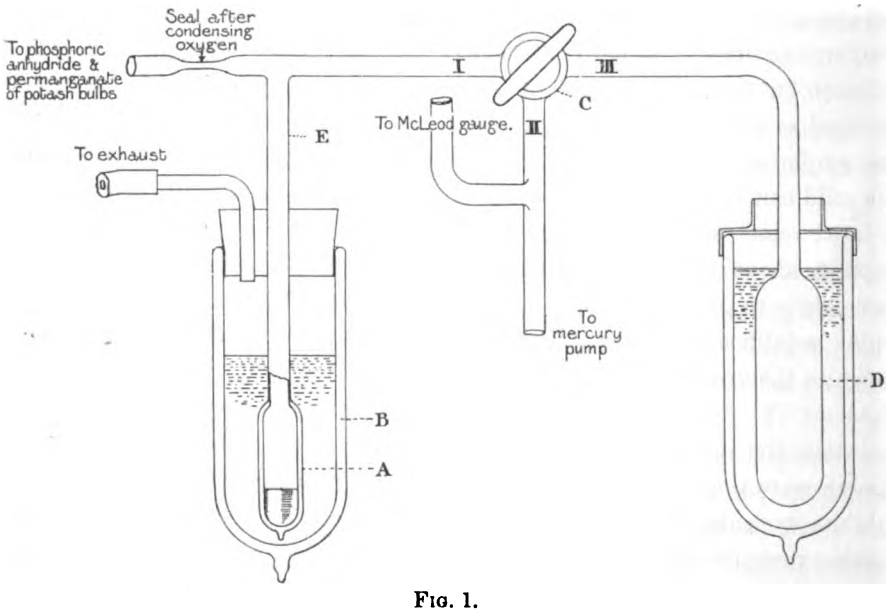

FIG. 1.

position ⊕, thus connecting I and II only, and the gauge, etc., can then be more thoroughly exhausted (to 0·0001 or less) by continuing the mercury pump. The permanganate bulb is now gently heated after closing off the mercury-pump cock, and the apparatus filled up with oxygen to near atmospheric pressure; this is repeated three times with intermediate exhaustion by the mercury pump. Liquid air is now admitted to B, which is then placed under exhaust. On heating the permanganate crystals, oxygen is now condensed in A. When sufficient liquid is obtained (about 8 c.c.) the permanganate and phosphoric anhydride bulbs are sealed off. The mercury-pump cock is now opened and the liquid oxygen in A well exhausted. This lowers the pressure to the order of 0·7 mm. in about 20 minutes or less.

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Meanwhile the charcoal bulb D has been cooled in a vessel of liquid air, or if a higher efficiency is wanted the liquid air may be exhausted. The mercury-pump cock is now shut off and the cock C is turned to position ⊖, connecting I, II, and III, whereby the exhausted oxygen is placed under the action of the charcoal, and the resulting pressure communicated to the gauge. In about 10 minutes or less the pressure falls to below 0·4 mm. and solidification occurs. By maintaining the charcoal exhaust the pressure on the solid oxygen can be reduced to 0·2 mm. in about 30 minutes. The real melting pressure of the oxygen is observed by turning C to position ⊕, connecting I

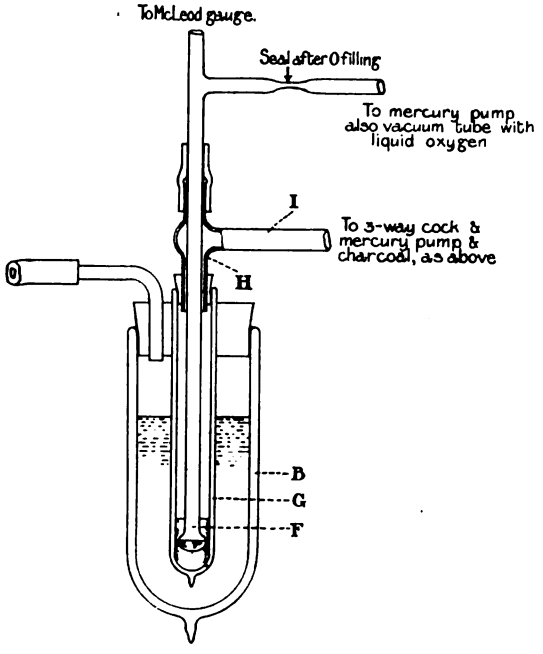

Fig. 2.

and II, the charcoal being thereby closed off, and the solid oxygen connected to the gauge alone.

In fig. 2 the arrangement is somewhat altered. F is a bulbed tube sealed on to a T-piece which connects to the McLeod gauge, and also, through a constriction, to a vacuum vessel of pure oxygen arranged in the mercury-pump circuit. By this means the gauge is filled to atmospheric pressure with pure oxygen evaporated from the liquid in the connected vessel (after filling and exhausting to 1 mm. by the mercury pump). The liquid oxygen vessel is then sealed off.

A glass tubulated fitting H is fixed by an indiarubber joint on to the bulbed tube F. The side tubulure of H connects to the three-way cock, etc., as in fig. 1,

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except that the connection for the McLeod gauge there shown is sealed off. A silvered narrow vacuum tube G provided with a slit is attached to the lower neck of H by an indiarubber cork. The whole arrangement is isolated by a vacuum vessel B containing exhausted liquid air as in fig. 1. About 10 c.c. of liquid oxygen are introduced into G (obtained by condensing oxygen from permanganate of potash in a separate tube in liquid air). The oxygen in G is now exhausted by the mercury pump and finally by charcoal as above, whereby the oxygen in the gauge is condensed in F and its pressure observed.

Some earlier determinations were made in which liquefied permanganate oxygen contained in a vacuum tube as G was simply connected to E (fig. 1) by a pierced indiarubber cork instead of the sealed-on vacuum tube A. This arrangement also works perfectly well for obtaining solid oxygen and observing its pressure, but is not adapted for liquefying oxygen direct from permanganate of potash.

In all cases the charcoal must first be thoroughly exhausted at about 300° C. by the mercury pump.

The pressures observed were as follows:—

5 to 6 c.c. of oxygen, in unsilvered vacuum tube connected by rubber cork, and isolated by exhausted air.

The limit of the mercury pump exhaustion on liquid oxygen, after 10 minutes, was 1·015 mm.

Charcoal exhaust connected—

Time in minutes	5	15	20	30
Pressure in mm. of mercury	0·323	0·30	0·2964	0·2964

The oxygen solidified in 10 minutes.

Solid oxygen on to gauge (charcoal off)—

Time in minutes.....	at once	5	10	20
Pressure in mm. of mercury	0·5372	1·165	1·813	2·013

The oxygen was still completely solid after 5 minutes. In 10 minutes about one-fifth had melted. In 20 minutes only very little solid left.

By starting the mercury pump again the pressure was lowered to 0·747 mm. in 10 minutes without solidifying the oxygen.

On again connecting the charcoal exhaust, solidification was accomplished in 10 minutes, the pressure being then 0·325. By allowing the charcoal exhaust to continue, the pressure on the solid oxygen was lowered to 0·302 in 30 minutes and 0·268 in one hour.

On again connecting the solid oxygen to the gauge the pressure was 0·613

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observed at first, rising steadily to 1·91 in 10 minutes, the oxygen being allowed to remain undisturbed.

Another series was carried out, using a silvered vacuum tube to contain the liquid oxygen, this being isolated by exhausted liquid air at a pressure of about 20 mm., also contained in a silvered vessel.

The mercury pump exhaust on the liquid oxygen, in 10 minutes, was 0·741 mm., without producing solidification.

Charcoal exhaust connected—

Time in minutes	3½	10	20	30
Pressure in mm. of mercury.....	0·3133	0·3384	0·2938	0·2492

The oxygen was completely solid in 3½ minutes with the better isolation afforded by the silvered vacuum tubes.

The solid oxygen connected on to the gauge at once gave a pressure of 0·467 mm. and 0·830 mm. in 2 minutes.

The charcoal exhaust was again connected, and produced solid as before, the pressure falling to 0·265 in 15 minutes. On again connecting the solid oxygen to the gauge a pressure of 0·43 was obtained, rising to 1·16 in 6 minutes, when solid was still largely present.

In the above observations the tube containing the solid oxygen was not agitated in any way, as by tapping, etc., during the readings. In the following observation this was varied.

Observations were made with a sealed-on vacuum vessel, as in fig. 1, the oxygen being directly liquefied from heated permanganate of potash. An arc lamp was arranged to illuminate the oxygen, using a parallel beam; a water cell being interposed to screen off heat radiation. The vessels used were silvered, with narrow slits to allow their contents to be observed. Further, to reduce the effect of supercooling and to maintain the liquefying or melting oxygen as far as possible at a uniform temperature, and consequently steady pressure, the vacuum vessels were, at the times noted below, kept well agitated by frequent tapping. This resulted in practically a steady pressure being recorded while the solid oxygen was melting.

Nearly 8 c.c. of oxygen was condensed. The mercury pump exhaust gave in 10 minutes a pressure of 1·471, and in 20 minutes 0·836, thereby evaporating about 1 c.c. of liquid.

Charcoal exhaust connected—

Time in minutes	5	15	30	40	60
Pressure in mm. of mercury	0·407	0·2492	0·1849	0·3384	0·2676

Owing doubtless to the larger quantity of oxygen dealt with, solidification did not occur until 31 minutes had elapsed, *i.e.* at a pressure a little lower

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than 0·185 mm. The pressure observed after 40 minutes, it will be observed, had risen to 0·3384, affording a distinct indication of supercooling. A later observation of such a pressure recorded below, made immediately after solidification, showed an even greater rise, viz., from 0·44 just before solid to 1·05 immediately after solidifying.

Solid oxygen on to gauge alone (no tapping) gave in this case :—

Time in minutes	½	2½	6
Pressure in mm. of mercury.....	0·4280	0·6471	0·8238

With charcoal again on, limit of pressure was 0·2072 in 25 minutes. On turning off the charcoal the oxygen remained quite solid for 15 minutes. The charcoal used in the condenser was now allowed to warm up to the ordinary temperature, when it only showed a pressure of 150 mm., due to the oxygen occluded at −180° in the above experiment. The same sample of oxygen (5 c.c. still left) was kept liquid in A for further observations. The charcoal was again thoroughly exhausted, and, on being again cooled, the following further observations were made, this time the oxygen bulb being well agitated, and illuminated as before.

Mercury pump exhaust was 0·778 in 20 minutes.

Charcoal exhaust connected—

Time in minutes	5	10	15	45
Pressure in mm. of mercury.....	0·4384	0·5948	0·4566	0·3078

Solidification instantaneous and complete in 11 minutes.

Solid oxygen on to gauge alone, well agitated.

Time in minutes	at once	7	10	15	20	25	30
Pressure in mm. of mercury...	0·465	0·94	1·107	1·112	1·159	1·142	1·150

No appearance of liquefying was evident for 8 minutes.

In 20 minutes about ½ c.c. of liquid was present, the remainder being a jelly, shaped to the containing tube and free in the small amount of liquid. In 30 minutes some 3 c.c. of liquid was present with a half sphere of transparent jelly.

In the beam of the arc lamp the oxygen was seen to solidify instantaneously, passing from a clear liquid to a slightly translucent mass. Under the continued exhaust of the charcoal the smooth surface of the oxygen became gradually broken up by numerous cracks penetrating but slowly down into the mass, and giving it the appearance of having a white crystalline surface. This disappeared very rapidly on turning off the charcoal exhaust, and the surface became quite smooth, although, with the good isolation, no appreciable melting could be detected for 15 minutes or more.

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It will be noticed from this last table of pressures that the tapping has resulted in reduced supercooling, since solidification was produced with a pressure of about 0·4 mm., compared with 0·2 mm. before. Also, the thorough mixing of the melting oxygen has resulted in concordant melting pressures being observed, as although readings were taken over 30 minutes, by which time a large proportion of the oxygen had melted, the pressure, having once risen to about 1·12, remained fairly steady, whereas when the melting oxygen was allowed to remain unagitated, the pressure as recorded before was always found steadily to increase.

Since the melting pressure thus appeared to be of the order of 1 mm. and also since the mercury pump reduced the pressure of the liquid oxygen to 0·7 mm., it was thought worth while to decide whether this pump could solidify the oxygen without having recourse to charcoal. For this purpose the action of the mercury pump was allowed to proceed for a longer time; the same sample of oxygen was employed. The following results were observed:—

Time in minutes	7	30	50
Pressure in mm. of mercury.....	1·065	0·824	0·721

No solidifying was accomplished, although the oxygen was well agitated. On connecting, however, the cooled charcoal, in 15 minutes the pressure was 0·44 mm., and while the gauge was being used to make an observation the oxygen went completely solid. Another reading was immediately taken, when a pressure of 1·048 was registered, distinct evidence of supercooling and a melting pressure of over 1·05 mm.

The oxygen thus being solid, the mercury pump was connected to it, and maintained the solid state, but did not lower the pressure below 0·75 mm., although allowed to run for some time.

The results obtained by the use of the apparatus fig. 2 are interesting. As described above, the gauge having been filled with pure oxygen, this is condensed in the bulbed tube F by cooling F in the solidified oxygen in G. The consequent pressures observed in the gauge were the following:—

Mercury pump on, thus exhausting 10 c.c. oxygen in G.

Time in minutes	10	20	30
Pressure in mm. of mercury.....	2·342	0·830	1·155

The pressure in G would undoubtedly be lower after 30 minutes' pumping than after 20 mins, yet the pressure registered in the gauge, *i.e.* of the oxygen in F, had increased between these two periods. This is similar to the supercooling usually obtained, but neither in F nor G had the oxygen yet solidified.

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Charcoal exhaust now connected, pressure in F as follows :—

Time in minutes.....	5	10	15	25	35	45	60
Pressure in mm. of mercury...	1·090	1·095	1·095	1·095	1·095	1·095	1·1035

The oxygen in the jacket G solidified in 5 minutes. That in F, however, remained liquid the whole time, but at an absolutely constant pressure. Apparently it was just not solid, and agitating was not sufficient stimulus to excite the solidification. The bulb F was 2 cm. below surface of the solid oxygen in G.

The remarkable constancy of this pressure seems to indicate that it is not very far from the real melting pressure. The pressure in the solid oxygen jacket G is undoubtedly falling, probably to a limit of 0·2 or 0·3 mm., through the action of the charcoal exhaust, yet the pressure in F is not altered, whereas if appreciable supercooling took place it would be shown by a continual lowering of pressure.

It is possible that the jelly was not in good contact with the bulb F, whereby the cooling effect would not be perfectly transmitted. Such a jelly or solid is a bad cooling medium, in the same way as solid hydrogen would not be a very good cooling jacket, liquid hydrogen at a little above melting pressure being preferable.

Estrecker has made observations both of the melting temperature and pressure of oxygen which had been solidified by the use of liquid hydrogen and allowed slowly to melt. The melting pressure observed was 0·9 mm., while the temperature of the melting point was 46° abs. It is interesting to calculate the pressure corresponding to the melting point either by the use of a Rankine or Willard Gibbs vapour-tension equation. Thus the Rankine two-term formula derived from Onnes' oxygen observations, viz. :—

$$\log p = 6{\cdot}9725 - 368{\cdot}3/T \text{ gives, if } T = 46°, p = 0{\cdot}092$$
$$\log p = 7{\cdot}0072 - 371{\cdot}2/T \quad \text{,,} \quad p = 0{\cdot}086$$

If $p = 1{\cdot}12$ mm., the corresponding T would be 53·3° abs.

Similar calculated pressures obtained from either a three-term Rankine or a Willard Gibbs are too low. If Onnes' three standard values of liquid oxygen temperatures and pressures are taken, then

$$\log p = 6{\cdot}2247 - 237{\cdot}83/T - 5694{\cdot}5/T^2 \text{ (Rankine)},$$

or $p = 0{\cdot}023$ when $T = 46°$ abs., and when p is $= 1{\cdot}12$ mm. the corresponding value of T is 55·2°. Also a Willard Gibbs, calculated from the same values, viz., $\log p = 12{\cdot}98421 - (464{\cdot}473/T) - 2{\cdot}52953 \log T$ gives a pressure of 0·048 mm., corresponding to $T = 46°$ abs. Further, a Willard Gibbs, calculated from the vapour pressures of oxygen given by Estrecker,

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gives $\log p = 16{\cdot}067 - 524{\cdot}7/T - 3{\cdot}802 \log T$, or $p = 0{\cdot}022$ mm., corresponding to $T = 46°$ abs.

Thus in every case the calculated pressure corresponding to the melting point of 46° abs. is considerably lower than the value observed, and, assuming the correct melting pressure to be 1·12 mm., the corresponding calculated melting temperature from these expressions would be as high as from 53° to 55° abs.*

By analogy, using a charcoal condenser to evaporate nitrogen or hydrogen in a similar manner to that described above for oxygen, we may confidently anticipate that the respective temperatures of 38° and 9° abs. might be reached. Doubtless liquid helium, which resists solidification by evaporation, would change its state when subjected to the action of a charcoal condenser cooled in liquid helium; and it might even succeed by the use of exhausted liquid hydrogen.

Mr. J. W. Heath, F.C.S., of the Royal Institution, and Mr. W. Green, B.Sc., of the Davy-Faraday Laboratory, have been of great assistance in the conduct of these experiments.

* *Note added November* 4, 1911.—Subsequent to the above experiments I determined the temperatures at the time of solidification by the use of a small hydrogen gas thermometer, and found the value 54° abs. In the meantime, Prof. Onnes has independently found the melting point of oxygen to be 54·6° abs. The Willard Gibbs extrapolation value is therefore very near the true temperature.

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Note on the Iridescent Colours of Birds and Insects.

By A. Mallock, F.R.S.

(Received September 12,—Read November 2, 1911.)

[Plate 11.]

Considerable interest attaches to the origin of certain forms of brilliant colouring which are of frequent occurrence in the animal world, though hardly represented among plants.* The colours in question are those which are not due to ordinary pigment, and which change with the angle of incidence of the light. The most brilliant examples are to be found amongst birds and insects. Fishes, and a few reptiles, exhibit colours of the same kind, but not so conspicuously.

During the last 10 or 12 years I have examined some hundreds of cases of this sort of colour production, and quite recently Michelson† has published investigations on the same subject, and refers to a somewhat similar paper by Walter, "Oberflächen und Schillerfarben," dated 1895, of the existence of which I was not before aware.

The conclusions of these authors are that the colours in question are, in most cases, due to selective reflection from an intensely opaque material, and, in some few, to diffraction from a finely striated surface. Their reasons for adopting the hypothesis of selective reflection rather than interference are the close similarities, as regards the reflection of polarised light, found between the natural iridescent colours and dry films of aniline dyes.

In the present note I give some reasons for the belief that, in the majority of cases, interference of some sort is the active cause; although, in others, the possibility of selective reflection is not excluded. The question really turns on the size of the "grain" of the colour-producing structure. Is it comparable with the wave-length of light or of molecular dimensions?

If the colours are due to interference, the first supposition must be true; but if selective reflection is the agent, a comparatively small group of molecules may cause selective reflection. It seems clear that this property cannot belong to individual molecules, at any rate in the case of the aniline dyes, for their solutions absorb impartially all the colours which are not transmitted, and it is only in the solid state that their peculiarities as regards reflected light become apparent; at the same time there is no change in the light transmitted, whether the dye is in solution or a dry film.

* Some Lycopodiums exhibit traces of iridescent colour.

† "Metallic Colouring in Birds and Insects," 'Phil. Mag.,' April, 1911.

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Before entering in detail into the reasons which seem to point to interference rather than selective reflection as the origin of iridescent colours, some general remarks may be made on the character of the structures examined.

These structures have been either feathers of birds or the scales of insects. There are few orders of birds in which examples of iridescent colouring cannot be found, but without doubt the humming birds are the most brilliant; although peacocks, trogons, and many others, are not very far inferior. In the insect world the finest examples are to be found amongst butterflies and the day-flying moths of the genus Urania. Some beetles also are provided with vividly coloured scales. These belong mostly to the weevils (which include the Brazilian diamond-beetle).

Many other insects among the Diptera, Neuroptera and Hymenoptera show brilliant metallic colours on their integuments, but these are not provided with scales, and in many cases the colour fades, more or less, when the specimens become dry. These I have not examined. Feathers and scales, however, are remarkable for the permanence of their iridescent colouring, and it is to these only that the present observations apply.

Some of the peculiarities of the structures, as regards change of colour with the point of view, depend on the shape of the surface on which the colour-producing material lies. If the surfaces are flat or nearly flat, reflection takes place as from a looking glass, and the angle through which the specimen can be turned while still showing the characteristic colour is small. Often, however, the surfaces are convex bosses or ridges, and then the angle of incidence and reflection is that contained between the direction of the incident light and the normal to the tangent plane at the point where reflection takes place, and is therefore to a great extent independent of the position in which the specimen is held, since there will always, within wide limits, be tangent planes to the convex surfaces which reflect the incident light in the line of sight. In these cases the colours might at first sight be taken as due to pigment, both on account of their comparatively low intensity and from the small change in tint and intensity which is produced by altering the inclination of the general surface to the direction of the illumination. The low intensity is of course due to the small area of each convex surface which reflects light in any given direction.

In attempting to investigate the origin of the colours many methods were employed, the first and most obvious being to cut thin sections normal to the colour-producing surface and then to examine them with the highest microscopic power available. If the colours are analogous to those of thin plates it is clear from the high intensity of the reflected light that more than one pair of surfaces must co-operate in the reflection. In general the reflected

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light is not even approximately monochromatic, and this fact limits the number of surfaces which can be supposed to act; but if the surfaces are supposed to be separated by air and placed at the most favourable intervals, their number need not exceed three or four to account for the observed intensity and tints.

The most favourable spacing for the successive layers is that their thickness and the intervals between them should be a multiple of the half wave-length of the mean ray, reckoned in the length of the waves within the material of the layer, and it was thought possible that the thin sections might show a laminated structure.

For the material of feathers and insects' scales, μ is somewhere about 1·5 or 1·6, so that the least thickness for the plates of refractive material would be of the order of 1/150,000 and the air intervals 1/100,000 of an inch—both beyond the resolving power of the microscope; but from the composition of the reflected light it seemed likely that the intervals might be two or three half wave-lengths, which would be readily seen as far as adequate separation of the images is concerned. In nearly all the sections examined bands of this order of thickness appeared with some forms of illumination, but it was impossible to be sure that they were not due to diffraction effects from parts of the section slightly out of focus.

There are many difficulties in preparing sections thin enough for the advantageous use of objectives with large angular aperture. When a section is to show a stratified structure its thickness should certainly not be greater than the distance between the successive strata, and may with advantage be much less. It was not difficult to cut sections about 1/20,000 inch thick, but this is three or four times too thick to show with certainty stratification whose pitch is 1/60,000 or less.

Occasionally, by accident, thinner sections (perhaps 1/40,000) would be cut, and these showed apparent stratification most plainly, but in no case was the image free from the effect caused by some part of the thickness of the section being out of focus, and, in all probability, what appeared to be stratification was in reality a series of diffraction bands. Insufficient thinness, however, is by no means the only obstacle to resolving the grain in the structure.

Thin sections are in general very transparent, and the only source of variation of intensity in the image formed by the microscope depends on the varying amount of retardation affecting the waves which traverse their different parts, that is (since the section is of uniform thickness) on differences of refractive index; but, in order to view such sections at all, it is necessary to mount them in some refractive medium, and this greatly reduces the chance of detecting a fine-grained structure.

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I have tried washing out the bedding material and examining the sections when dry, but, although great care was taken in keeping the cutting edge of the knife smooth and sharp, striæ always appeared in the direction of the cut, which quite obscured the real structure. The fact is, that there are very few objects on which the highest microscopic powers can be used with advantage. Even the test diatom, *A. pellucida*, which, of course, has to be mounted dry, or in a medium whose refractive index greatly exceeds that of silica, is too thick to give a satisfactory image, and small solids, whose dimensions are less than a wave-length, give images which are not their enlarged geometrical outlines, but phenomena depending on the wave-length.

Although the microscope, in my hands, at any rate, has failed to give direct evidence of a "periodic" structure, other tests point strongly to "interference" as the origin of the colours.

In some cases the colour-producing film is backed by an extremely opaque layer, and in others the whole of the structure is transparent, and transmits the complementary colour with nearly the same intensity as the colour reflected. Even where there is an opaque backing, this is often thin enough to allow of examination by strong transmitted light, and the prevailing colour is a brown, tinged with the unabsorbed complementary to the colour reflected. These opaque backings are present in most feathers and in some insect scales, but in the majority of cases the scales of insects are transparent.

Both theory and observation show that, when the reflected colour depends on interference, the tint will change towards the blue as the angle of incidence increases, so that reds become yellows, yellows change to greens, and greens to blues, and also that, if the colour-producing structure is immersed in a refractive fluid instead of air, the reflected colour will change towards red, and have its intensity reduced. Two causes are operative in producing this change: In the first place, if the colour-producing film is protected from the fluid by an impermeable outer layer, with which it is in optical contact, the only effect of the fluid is to diminish the angle of incidence of a ray of given obliquity in air, so that the colour reflected is that due to the smaller angle of incidence. Secondly, if the fluid penetrates the layers in which interference takes place, the interval between the layers, now reckoned in wave-lengths in the refractive fluid, is increased, and therefore also the wave-length which is reflected for a given angle of incidence. At the same time the intensity of the reflected light is greatly reduced, and, if the fluid has the same refractive index as the structure itself, reflection ceases and nearly white light is transmitted.*

* The dispersion of the fluid, as well as the refractive index, must be the same as that of the structure if the transmitted light is white.

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Observation of reflection from films of aniline dyes, etc., shows that the colour changes in the same direction, that is towards the blue, as the angle of incidence increases, but as regards the character of the change when the film is covered by a refractive fluid there is a great difference.

In some cases (methylene green for instance) for one particular angle of incidence the colour reflected in air is unchanged when the film is covered with cedar oil, for smaller angles of incidence the reflected light is of shorter average wave-length, and for greater angles longer than that of the colour in air.

For this particular dye the colour reflected in air is a very red-purple at small angles of incidence, changing to bluish-green when the angle is large.

Under cedar oil the colours are respectively greenish-yellow and an orange-yellow. The transmitted colour, however, does not change perceptibly either with the angle of incidence or with the medium in which reflection takes place, and this applies, as far as my observation goes, to all substances which give selective metallic reflection.

The transparency or, at any rate, the vanishing of the characteristic transmitted colour in the case of all animal tissues when immersed and permeated by a fluid of the same refractive index is strongly in favour of interference being the source of the colour, but even stronger evidence is given by the behaviour of the structures under mechanical pressure.

If the grain or peculiarities which favour the reflection or transmission of particular colours is of molecular size, there is no reason to suppose that pressure insufficient to cause molecular disruption would alter the action of the material on light. On the other hand, if the colours are due to interference, that is to cavities or strata of different optical properties, compression would alter the spacing of these, and thus give rise either to different colours or, with more than a very slight compression, to the transmission and reflection of white light.

In every experiment of this kind which I have made either on feathers or insect scales the effect of pressure has been to destroy the colour altogether.

Where the scales are transparent white light is transmitted, but with feathers, where the colour film is generally backed by dark pigment, the pigment colour appears untinged with the complementary to the colour naturally reflected.

With many feathers the colour returns when the pressure is taken off, but with insect scales the structure seems to be permanently injured by compression, and though when allowed to expand again the material is not

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colourless the brilliancy which belonged to the uninjured scale is gone, and the colour in general changed.

The facts above mentioned seem to offer stronger reasons in favour of interference than the polarisation phenomena referred to by Michelson and Walter* do against it.

The ellipticity, etc., found in the reflected beams may, although functions of the wave-length, accompany the production of colour without being necessary to it, that is, they may depend on the molecular while the colours depend on the mechanical structure.

All Lepidopterous scales, whether coloured by pigment or giving metallic reflection, are traversed by a series of fine lines or dots arranged in lines and very evenly spaced, and the universality of these lines on all such scales, whether with or without colour, is a good reason for not regarding diffraction as an explanation of the metallic colours.

In many insects these lines are as close as 36,000 to 40,000 per inch, and when light is transmitted through a single scale or a few scales placed side by side, very fine diffraction spectra are formed, but no corresponding effect is seen by reflection, what effect there may be being masked by the other form of colour production.

The beetle scales which I have examined were, as a rule, without linear markings, and where lines existed they were not very regular. The surface was always mapped out into unequal polygonal areas, and a cross section (Plate 11, fig. 5) showed that the scale consisted of a flattened sac of transparent material containing a cellular structure in which the colour originated.

When an unbroken scale is immersed in cedar oil, the outer walls prevent the fluid reaching the colour-producing layer and but little change results either in the reflected or transmitted light, but when the scale is broken or has a piece cut off the oil penetrates the interior and all trace of colour disappears.

Occasionally when a viscous fluid is employed the penetration is not complete and the character of the cellular layer is then indicated by the parts which still show colour.

Figs. 1 to 4, Plate 11, illustrate this. Fig. 1 is an unbroken scale of *Entimus imperialis* showing the polygonal areas. Fig. 2 shows the same scale partly penetrated by a solution of celluloid in amyl acetate. Fig. 3, ditto (in which the penetration is not so complete) more highly magnified. Fig. 4, three scales completely penetrated and quite colourless. Fig. 5 is a cross-section of the scale (thickness of section about 1/20,000 of an inch).

Feathers are impermeable to most fluids, but when acted on by acid (nitric,

* Polarised light should be used for this observation.

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acetic, or hydrochloric) they change colour towards the red; after washing and drying, however, they regain their original tint.

The subjects from which the above notes have been made include among birds, various species of humming-birds, peacocks and pheasants, sun-birds, trogons and others; among Lepidoptera, the genera Euplœa, Morpho, Calligo, Argynnis (in which silver markings are common), Vanessa, Callicore, Lycæna, Thecla, Papilio, Ornithoptera, some of the Hesperidæ and moths of the genus Urania. The only beetles examined were *Entimus imperialis* and two species of Cyphus.

To the physicist who is also a naturalist, the great variety in the character of the surfaces on which these metallic colours are developed, as well as the beauty and brilliancy of the colours themselves, offers matter of exceptional interest, but it would occupy too much space to enter here into a detailed description of even the typical forms.

A rather curious fact, however, may be mentioned with regard to the scales of Lepidoptera. Nearly all such scales when black or coloured by pigment have the free end deeply scalloped and presenting what may be called an ornamental outline, but the scales which show metallic reflections are invariably (as far as my observation goes) merely rounded off or have very slight indentations. Figs. 6 and 7 (which are respectively coloured and black scales from *Ornithoptera Poscidon*) illustrate the difference.

Although all the colours referred to in these notes are probably the result of interference, the ways in which the interference occurs may be very various. Feathers, by their behaviour, suggest an action analogous to that of a Lippmann film, but it is difficult to imagine matter optically dense enough to behave as the silver particles in the film being produced in an organic structure. In most of the scales it seems that the interfering rays are reflected from the surfaces of very thin flat cells, but it is possible that, in some cases, the effect may be due to reflection from a single dimpled surface. The coloured central images sometimes given by diffraction gratings are examples of this sort of interference, but in order that the colours so formed should be as brilliant as possible the depressions or dimples should be closely but irregularly distributed over the surface (if regular much of the light goes in lateral spectra), but of uniform depth and section. I have succeeded in making coloured rings of some brilliancy by holding a piece of glass over the smoke of an arc formed between metal electrodes, iron, nickel, silver and copper being used. In the most successful trials the rings were brighter than the colours of soap films, and, as might be expected, the intensity of the colour increased with the angle of incidence, but the rings did not show with normal reflection, nor until the incidence exceeded 30°.

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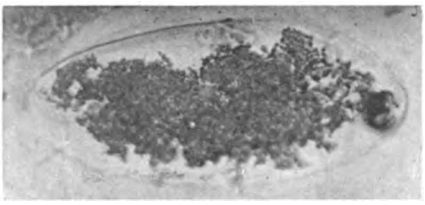

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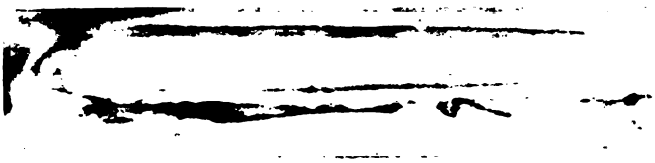

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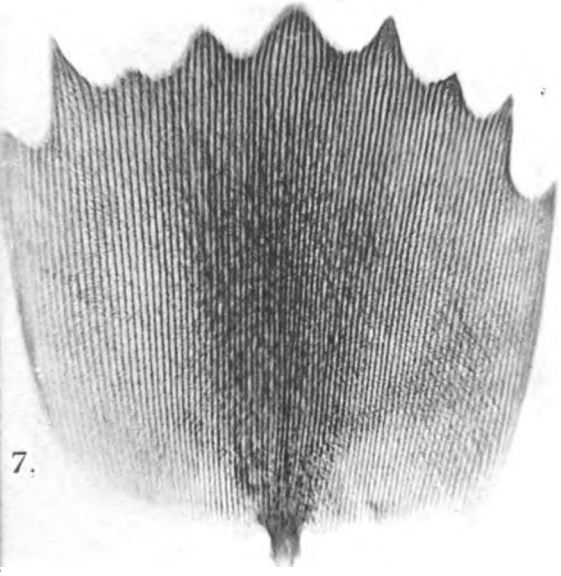

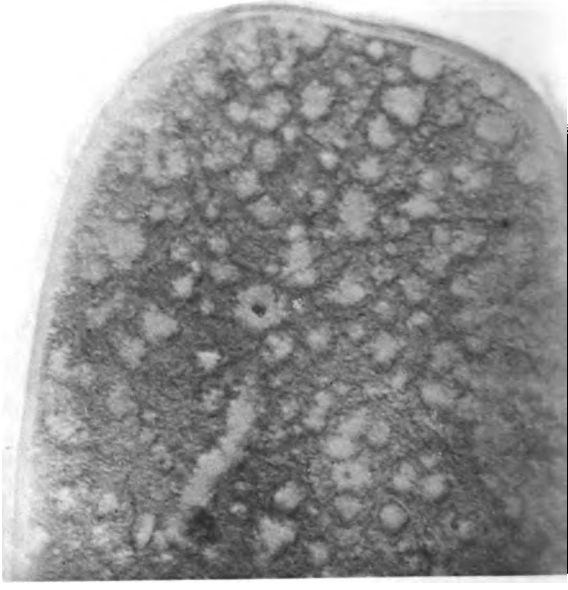

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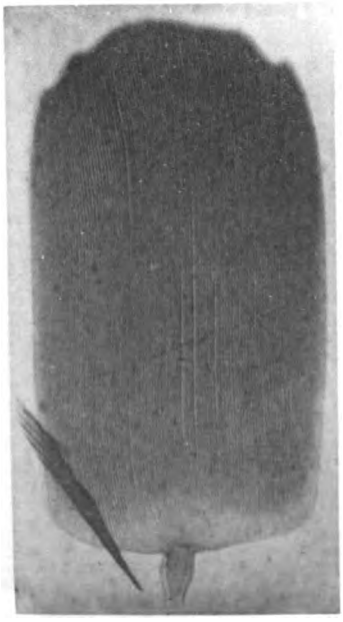

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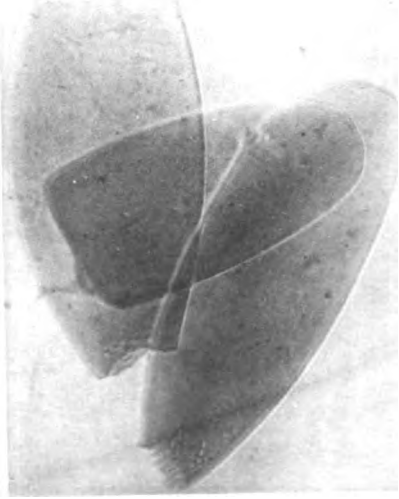

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In the spectroscopic examination of the colour, it was found convenient to focus the much enlarged image of the surface on the slit of the spectroscope. By this means, and using the sun or an arc lamp, there was sufficient light to show the spectrum from a small part of a single scale.

When cutting thin sections of chitin or feathers it is important that the embedding material should be of the same consistence and hardness as the object to be cut. For this purpose shellac gave the best results. The hardness could be regulated by the time allowed for drying.

The compression tests were carried out by placing the specimens on a slide under a convex lens of about a foot radius. The objects compressed were generally thin enough to allow of the Newton rings of the higher orders being recognised between the lens and slide before any compression occurred, and by centering the object in these the pressure could be applied in the right place.

Since writing the above, I have examined the colours of some of the iridescent Diptera (chiefly of the genus Lucilia), using the pressure apparatus. It was found that with them, as with the scales and feathers, the colour disappeared under compression, and it seems probable, therefore, that interference of one kind or another is the true cause of natural iridescent colour in all cases. It may be remarked that the intensity and composition of the light reflected from the integument of the flies is such as would be accounted for by the interference of a single film or pair of surfaces.

DESCRIPTION OF PLATE.

Fig. 1.—Scale of *Entimus imperialis*. × 490.
Fig. 2.—The same partly permeated with celluloid solution. × 490.
Fig. 3.—The same. × 1750.
Fig. 4.—Three scales of same completely permeated. × 490.
Fig. 5.—Cross-section of scale. × 1750.
Fig. 6.—Iridescent scale of *Ornithoptera Poseidon*. × 1170.
Fig. 7.—Black scale of same. × 1170.

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WILLIAM EDWARD AYRTON, 1847—1908.

PROF. AYRTON was born in London on September 14, 1847, and he died November 8, 1908. He was elected to the Royal Society in 1881, and he was awarded a Royal Medal in 1901.

He was the son of an able barrister, Edward Nugent Ayrton, and the nephew of the Right Hon. Acton Ayrton, who was a member of Mr. Gladstone's Government from 1869 to 1874. He belonged to a family which for three hundred years had been represented by lawyers, musicians, surgeons, clergymen, university dons, and schoolmasters. He distinguished himself at University College School, and later at the College; he gained the Andrews Exhibition in 1865, and the Andrews Scholarship in 1866. In 1867 he passed with honours the first B.A. examination in the University of London; in the same year he came out first in the examination for the Indian Government Telegraph Service, and in preparation for India he became a pupil of Lord Kelvin in Glasgow. In India, after acting as assistant to Mr. Schwendler, he succeeded him as Electrical Superintendent of the Telegraph Department; these two men revolutionised the Indian telegraph system. In 1872–73 he was on special duty in England, and assisted Lord Kelvin and Prof. Jenkin, the engineers for the Great Western Telegraph Cable. From 1873 to 1878 he was Professor of Natural Philosophy and Instructor in Telegraphy in the Imperial College of Engineering, Tokio, Japan. From 1879 to 1884 he was Professor of Applied Physics at the City and Guilds Technical College, Finsbury, and at the same time he had much practice as an engineer. From 1884 till he died he was Professor of Applied Physics and Electrical Engineering at the City Guilds Central Technical College, Kensington. An active member of the Institution of Electrical Engineers almost from the beginning, a diligent member of Council and of the Committees of the Council, he became President in 1892. He was President of the Physical Society of London in 1890 and 1891, and President of Section A of the British Association in 1898. He served on Juries at various exhibitions, and as a member of various Congresses dealing with international electrical questions.

A complete list of his scientific papers will be found published in the memorial number of 'The Central' (the Journal of the City Guilds Central Technical College) for April, 1910. Eleven of these were published by him before 1876; sixty-eight in partnership with Prof. Perry between 1876 and 1889; during this interval there were also sixteen in his own name or occasionally in partnership with other workers; after 1889 he published fifty-one papers, many of them in partnership with Prof. Mather, Dr. Sumpner, and others. He was joint editor with Dr. Wormell of a series of Manuals of Technology in 1881, and he wrote one of these Manuals on 'Electric Lighting and Transmission of Power.' Later this book, greatly altered and added to, took the new title 'Practical Electricity.'

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His work previous to 1874 lay in improving telegraphic methods, especially those employed in India. During his first year in Japan he arranged an electrical laboratory, which was certainly the finest then existing in the world. A description of it will be found in a paper read before the Society of Arts in 1880 by Prof. Perry. Even in 1874 he was carrying out the idea that not merely for a few students, but for all of his students, laboratory work was the essential thing, and that lectures and numerical exercise work were the auxiliary things in a scientific education.

His students were very earnest and hardworking, and they became enthusiastic about laboratory work, especially in electricity. Prof. Ayrton was himself intensely fond of experimental work in electricity; he used often to work throughout the night and throughout the long and very hot or cold holiday time in Japan. Readers must remember how very different things were from 1874 to 1878 from what they are now. At the forty-one consecutive meetings of the Royal Society from December 11, 1873, to May 13, 1875, there were in all only five papers read which had a bearing on electricity; indeed, there were not many electrical experimenters in the world, and the Japanese investigations from 1875 to 1878, published in numerous papers read before the Royal Society, the Physical Society, the Institution of Electrical Engineers, and elsewhere, attracted a great amount of attention not only from scientific people, but from many other persons whose imaginations were beginning to be stirred by the importance of the telephone, the dynamo machine, and the electric light.

After his return to England, Prof. Ayrton arranged an electrical laboratory at the Finsbury Technical College, intended for evening students who were workers in electrical engineering industries, and also intended for large classes of day students. This laboratory and his methods have been copied by hundreds of Polytechnics and technical schools, and it is well here to state precisely in what way he made a new departure. Long before he went to Japan, some of the students attending Physics lectures in many parts of Great Britain had been doing laboratory work, but in every case these students were very clever volunteers. Ayrton gave interesting laboratory work to *all* his students. The motors and dynamos and other contrivances which were tested were not so small as to be toys, and they were not so large but that they could be left in charge of the average student without fear of disaster. But it was the preliminary work that was particularly his invention. In the study of mechanics and other parts of physics we deal with weight, inertia, stress, colour, space, etc., and his senses make such things tangible to a student; but in electricity we deal with something almost abstract, and there must be a regular training which will make the things which we call current and voltage and resistance and magnetic induction just as tangible to the student as weight is. Such laboratory practice as had hitherto existed was for the clever student. Prof. Ayrton recognised that the *average* student usually learnt nothing whatever, because there was usually no attempt to make these ideas familiar to him. Hence he not only

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insisted on giving laboratory work to every student, but determined that the object of much of the work should be to familiarise the student with the most elementary notions. Thirty years have elapsed, and many of the teachers who use apparatus and laboratory arrangements copied from Finsbury are not yet aware of the futility of trying to teach the average student through unfamiliar abstract ideas. All throughout his life, Prof. Ayrton was afraid of talking over the heads of his hearers, of assuming that because an idea was familiar to himself, it was therefore familiar to them.

Again he never tried to produce the perfect engineer. He aimed at creating a learner, a person of developed common sense, a man who would learn engineering when he had the chance of practice, a man whose education would go on till he died; a man who could use books, a man fond of reading. It is difficult to say how much of his system is due to his colleagues at Finsbury. They had the same ideas, they never quarrelled, they never seemed to differ in opinion; on any given question they seemed always to come to the same conclusions. No mere chemist taught chemistry, no mere mathematician taught mathematics, no mere physicist taught physics, no mere specialist taught anything at that college. Every subject was taught through the other subjects. There was no examination from the outside and there was no pretence of preparing men for examinations. No marks were given for lecture notes; but rough laboratory notes and finished accounts of laboratory work in good English, with elaborate sketches and squared paper curves, were thought most important. As hundreds of students passed through laboratories of no large dimensions in one week, and as the number of instructors was very limited, it was impossible on any system whatsoever to give instruction which satisfied the Professor; but at any rate the average student really did learn something and was eager to work, and it was found possible to give great encouragement to any student who adventured and discovered things of which he had not been told. Advanced students had fine opportunities for original research. In dealing with students, that earnestness and enthusiasm and inspiration, that training in scientific method, that sympathy and helpfulness for others which Ayrton received from Lord Kelvin, he handed on to many thousands of pupils, and they in turn are handing them on to new generations.

In 1884, when he became Professor at the Central College in Kensington, he, for the third time, arranged an electrical laboratory. The money available being as great as what he had in Japan, his own experience being much greater and quite different, and the position of the study of electricity being recognised as having become one of enormous importance by the industrial world, it became what it now remains—a most perfect laboratory. There are in existence laboratories with larger and much more expensive equipment, but size and cost in a college laboratory are poor things in comparison with fitness for educational purposes.

Till 1884 and later Prof. Ayrton was not only the most important teacher of applied electricity, he was one of the very few great pioneers in the

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development of electrical engineering; his students knew that they listened to a man whose days and nights were filled with success in invention and discovery. There are now hundreds of good schools of electrical science; in most of them Ayrton's pupils are teaching. There are now thousands of electrical engineers in whose employment a man can obtain experience. But before 1884 there was only one school, there was almost only one office in which, and there was almost only one engineer in whose service, education and experience could be found. Many young men of promise were attracted from Germany and America and elsewhere to the place where new discoveries and new inventions were the order of the day. Those discoveries are now such common knowledge, those inventions are such usual parts of all electrical machinery, that nobody dreams of mentioning their author's name in connection with them.

He not only read papers at The Institution of Electrical Engineers, but he looked after the interests of that Society with the care of a parent. His contributions to numerous discussions were always well prepared and ought to be read by all who are interested in the history of electrical engineering.

He was particularly successful as a public lecturer—first, because he never lectured on worn-out subjects, but on those which had been greatly developed by himself, and were of great popular interest; second, because he had made a study of elocution, and he had cultivated a particularly good voice; and thirdly, because he spared no pains in preparing his addresses, and in arranging his experiments. But, indeed, all his work was thorough; he was not only a man of large ideas, he was also a man who was a master of detail and who worked hard continuously, so that his success was well earned.

Of the numerous investigations in Japan the most important were on the potential differences between substances in contact; the properties of dielectrics, and particularly their behaviour as electrolytes; heat conductivity in stone; the explanation of the "magic" properties of certain Japanese mirrors; the measurement of v, the ratio of the electro-magnetic to the electro-static unit of electric quantity; the theory of continuous beams, &c. Work on some of these subjects was continued in England, but till 1886 most of the publications relate to inventions of instruments such as sets of permanent magnet and other instruments to measure electric current and voltage, self and mutual induction, etc. The most important inventions were the clock and motor methods of metering the supply of electricity to houses, and these methods are almost the only ones now in use. There were also improvements in dynamo machines, and especially in electromotors; a dispersion photometer; spring balances; resistances for use with strong currents, varied by foot and hand; the power-meter; ohmmeter; a non-sparking key; switches for use with accumulators and arrangements for lighting railway trains; photometers; dynamometer couplings and transmission and absorption dynamometers; an electric arc lamp; the governing and regulation of motors and dynamos; an electric tricycle; an electric

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railway system with friction gearing, contact boxes, locomotives and automatic blocking, forming part of the general telpherage system; seeing by electricity; a multi-reflex arrangement for measuring the angular motion of a mirror; a ballistic galvanometer, &c. Two very important inventions were a magnifying spring and a twisted strip. Many of these inventions were described in papers read before scientific societies; many of them are in general use now in electrical engineering. Many papers published till 1889 describe investigations on the electric arc; the most economical potential difference to use with lamps, economy in electrical conductors, the expansion of mercury between 0° C. and −39° C., efficiency of lamps with direct and alternating current, the efficiency of transformers, the practical unit of induction, the study of accumulators, photometry, the index of refraction of ebonite, measurement of the ohm, the economical use of gas engines, the distribution of electric energy, electric railways, the electric resistance of liquids, the theory of beams fixed at the ends, the driving of dynamos with short belts, the magnetic circuit of dynamos.

From 1890 until his death his inventions had less to do with practical engineering; a new quadrant electrometer, the credit in which is shared with Dr. Sumpner; numerous instruments used in his new laboratory; a variable inductance standard; the Ayrton-Mather galvanometer; a magnetic field tester; a universal shunt; transparent conducting screens; air choking coils; a new current weigher, the credit of which was shared with the late Prof. Viriamu Jones, and many other inventions.

Papers were published describing these and other laboratory instruments, as well as investigations: thermal emissivity of thin wires in air, measurement of electric power, on glow lamps, non-inductive resistances, efficiency of transformers, the electric arc, speed and voltage in electric motors, submarine telegraphy, the ohm, sensibility of galvanometers, permanency of resistance coils, on smell, dielectric hysteresis, the cadmium cell, etc. He contributed five important articles to the Engineering Supplement of 'The Times.' He published many papers and addresses on educational subjects.

In all his laboratory work at Finsbury and Kensington he greatly relied upon the collaboration of Mr. Mather, who is now his successor, and he was always ready to declare his gratitude for the assistance of that very gifted man.

The most active time of Prof. Ayrton's life was that in which he was one of the very few men who were developing electrical engineering. Later, when there were many men creating new electrical industries, he saw that his best work lay in the improvement of laboratory methods and instruments, and particularly in the education of his students. Perhaps it is wrong to say that he was less active than before. In the memorial number of 'The Central,' above mentioned, some of his pupils tell of the enthusiasm which he created. Even the average student was lifted out of his petty life of care about examinations, and saw that there was a higher life, and not only this,

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but his methods of observing and working and thinking became truly scientific. As for the exceptionally clever students they received an inspiration which is placing them higher and higher among scientific workers. As Mr. Maurice Solomon has said, the first few weeks of Prof. Ayrton's teaching came as a revelation to students, for "the nightmare of the text-book and the methods of the crammer vanished into the limbo of the past."

Mr. Solomon proceeds:—"Though lectures and exercise classes necessarily supplemented the work of the laboratory, they were based as far as possible on the laboratory work, and the student was always made to feel that it was the experience which he was gaining in experimental work which would be of value to him in after life, rather than the actual knowledge of facts which he was acquiring. And to this end also may be traced the far greater importance attached to the reports on experiments than to the transcript of lecture notes or the working out of mathematical examples. On the reports drawn up by the senior students on their research work, Prof. Ayrton brought to bear the whole weight of a strong critical faculty, and there must be many of his students who recollect, possibly with mixed feelings, the care and thoroughness with which he would examine their accounts of their researches. For those who were fortunate enough to have been engaged on some piece of valuable original research no trouble was too great; each argument was examined step by step, each method was examined step by step, each method was discussed from all sides to make certain that no flaw could be discovered in the structure, and that no loop-hole for error existed. The papers which have been published by his students, both during and after their College days, bear eloquent testimony to the thoroughness of these methods. And the files of the College contain as much unpublished work of a similar character and of almost equal value, work that remains unpublished because the men have been wanting to carry to their conclusion the researches of their predecessors, or because it has been laid aside on account of 'so many other interesting things to attend to.'

"Much of the spirit which permeated the teaching at the College was due to the principles on which that teaching was based, principles which have since been extended to other institutions and other subjects. But much also was due to the personalities of the exponents. Prof. Ayrton deserves truly to rank as a teacher of the first water: it is a quality only to be judged by the effect upon the students. As a great headmaster moulds by almost imperceptible influences the characters of those who pass through his school, so that his reputation lives and survives, not because of some thing or things that he has done and that can be recorded, but in the tradition that passes down the generations of his pupils, so did Prof. Ayrton influence and mould his students. He was able to impart to them some at least of his own enthusiasm for his subject, and to awaken any powers that were latent to their full development and fruition. If you would gauge

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the full effect of Prof. Ayrton's work you must not look to the record of the distinguished positions he has held, to the list of his inventions, or the tale of his publications; you must not look even to the positions which are held by those who have been his students; you must look rather to the methods in every electrical factory or undertaking in which his students have played a part, and there you will find that in a greater or lesser degree according as the instrument was more or less worthy, his teaching has had its influence, and that some part of the success and prosperity is due to him. Whether for laying many of the foundations on which it has been built, or for providing a supply of rightly trained, capable, and enthusiastic builders, there are few men to whom the electrical industry of to-day owes a greater debt of gratitude than to Prof. Ayrton."

In the same memorial number we find the following:—

"Abundant initiative was another prominent feature of his character, and his influence on colleagues, assistants, and students in this direction was very marked. He had the gift of interesting those about him in original work, and of inducing them, both by example and precept, to follow such work to a successful issue.

"Unlike some investigators, Prof. Ayrton was always anxious that his assistants and students should participate in the credit resulting from any research in which they had taken part, and this accounts in a great measure for the large number of joint papers for which he was mainly responsible.

"To be associated with him in a piece of original work, or in a patent case or Parliamentary inquiry, was indeed an education in itself, for the logical and methodical manner in which the subject was considered in all its bearings, and the thorough and painstaking way in which the results or evidence were criticised and checked before being accepted, was remarkable. No amount of trouble was too great for him to take to ensure accuracy, and things which to others might appear trivial were fully examined in detail, for to him thoroughness was an essential factor in everything.

"As a chief he was ever thoughtful and considerate for his subordinates, but at the same time expected whole-hearted work from each and all. Never sparing of himself and always willing and eager to assist and encourage others in any work they were engaged, he took a particular pleasure in helping others to help themselves.

"Independence of thought and action always commanded his interest and appreciation, whilst unreasoning imitation was severely criticised on many occasions.

"The encouragement of his pupils to think for themselves and to examine critically the statements of even recognised authorities were cardinal features of his teaching, and 'to follow the crowd' in any matter was foreign to his nature."

He married his cousin, Matilda Chaplin, one of the famous Edinburgh medical students who may be said to have been the martyrs in the cause of women's higher education. She was energetic, artistic, literary and scientific,

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and they were sympathetic partners. She studied in Dublin and became a licentiate of the Royal College of Physicians. She studied in Paris and took her M.D. degree in 1879, her thesis being an account of elaborate scientific work done by her in Japan. Their daughter, Edith, now Mrs. Israel Zangwill the writer, was born in Japan. His second wife was Miss Marks, a distinguished Girton student; she was awarded the Hughes Medal of the Royal Society in 1906 for her long continued experimental investigation of the electric arc and her work on sand ripples. Their daughter, Barbara Bodichon, now Mrs. Gould, is distinguished as a public speaker.

J. P.

BINDON BLOOD STONEY, 1828—1909.

BINDON BLOOD STONEY was born at Oakley Park, King's County, on June 13, 1828. He was the second son of George Stoney, B.A., of Oakley Park, in the King's County, and of Anne, second surviving daughter of Bindon Blood, D.L., of Cranagher and Rockforest, in the County Clare.

In the University of Dublin he graduated in Arts and Engineering. In the Faculty of Arts he was distinguished as a mathematician; and in Engineering he was the foremost man of his class, and won, without a single exception, the first of every distinction then conferred in that Faculty.

Family affairs having rendered it difficult, if not impossible, for him to follow up his University course in the usual manner by serving a term of apprenticeship to some distinguished engineer, he commenced work by taking the place of his brother, George Johnstone Stoney, at the Observatory of Lord Rosse at Parsonstown, where he made his mark by the excellence of the astronomical work he accomplished, and especially by making more accurate delineations of nebulæ than had before been obtained, and which continued to be among the best until, at a subsequent period, all eye observations were superseded by photography.

One of his achievements was ascertaining by eye observations the spiral character of the great Nebula in Andromeda, a discovery which he made in the early fifties of the last century, long before the days of astronomical photography. His work under Lord Rosse and another small employment occupied his time until he obtained, under Mr. Greene, his first professional engagement in laying out railways in Spain. There Mr. Bindon Stoney laid out one of the main lines.

He successively held the following appointments: Assistant Engineer on surveys for Spanish railways, 1852—1853; Resident Engineer on the Boyne Viaduct, 1854—1855; Assistant Engineer, Port of Dublin, 1856; Executive

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Engineer, 1859; and Engineer-in-Chief, 1862, which last appointment he held until 1898, when he retired after forty-two and a-half years' service.

When appointed as Assistant Engineer to Mr. James Barton on the Boyne River Viaduct he brought to bear on his work the scientific training he had received at Trinity College, Dublin, one of the first Universities to establish a School of Engineering. That structure, the Boyne Viaduct, was the first of its kind in which, upon a large scale, the strength of each part was accurately proportioned to the stress it had to withstand; thus saving material and, by reducing the weight, avoiding all the useless stresses which are prominently and mischievously present in all earlier viaducts. The safety of the structure was increased, as well as the length of span over which it could be erected.

It is reasonable to assume that his connection with the Boyne Viaduct led up to the writing of his classical work on the "Theory of Stresses in Girders and Similar Structures," which in its time was an epoch-making work, and went through many editions at home and in America, and with which his name will ever be associated.

He was appointed Assistant Engineer to the Port of Dublin in 1856, and in 1859 was called upon to act as Executive Engineer; in 1862 he was appointed Engineer-in-Chief, and it was in this position that his brilliant constructive powers were exhibited to the best advantage.

The Port of Dublin at that time was a tidal harbour with a shallow approach channel from the Bay to the city. In dredging out this channel he broke away from precedent and designed a large dredging plant, including harbour barges of the capacity of 1000 tons for conveying the dredging material out to sea. The economy thus effected allowed the Port Board to press forward the improvement of the approach to the Port of Dublin, so that at the completion of his work it was no longer a tidal port but open at all states of the tide to vessels engaged in the cross-channel and coasting trades, which form by far the larger portion of the total trade of the Port of Dublin.

He rebuilt a length of 6825 feet of quay walls, equal to half the shipping quays of the port, and replaced the tidal berths by deep-water berths at which large over-sea vessels could lie floating at all tides. The northern quays were extended eastward and the Alexandra Basin begun. To avoid the necessity of costly coffer dams and pumping, he built the lower portion of these quay walls with concrete masonry blocks of 350 tons weight. The blocks were of such a size that when one end rested on the bottom, the other reached low-water level, so that the masonry that had to be added was all of it subaerial work. The immense blocks were unlike ordinary concrete. They consisted, for the most part, of irregular masses of rock of great size, so placed that they touched one another at but few points, and were everywhere else firmly bound together, and to the rest of the structure, by fine concrete poured in between them. A special machine for making the fine concrete was designed by Mr. Stoney, which has since come into general use wherever large quantities of concrete are required.

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The blocks were built on a platform, and when sufficiently hardened were lifted by specially designed floating shears and transported to the site of the new quay. All machinery for handling these blocks, and the gigantic diving bell for laying the foundations, were designed by him, and were fully described in a paper which he contributed to the Institution of Civil Engineers, and for which he received the Telford Medal and Premium.

Among the many other works carried out by Mr. Stoney, the levelling and widening of the bridges over the River Liffey within the City of Dublin may be referred to on account of the special advantage which this work conferred upon the citizens.

A marked characteristic of Mr. Bindon Stoney's work as an engineer was the correctness of his engineering estimates. The actual cost of the work was, in each instance, nearly identical with that which he had been able to compute, thus avoiding the necessity for supplementary estimates. This reliability will be appreciated by all who have had experience of extensive engineering works.

Mr. Stoney retired from the service of the Port of Dublin in 1898, in his seventy-first year, respected for his engineering ability, unswerving integrity, and love of truth and justice, and regretted by all of his staff.

No record of Mr. Bindon Stoney would be adequate without some reference to the remarkable degree in which he was helpful to others throughout his long career, and amongst these to the many engineers whom he encouraged and helped forward in the early stages of their profession.

He was elected a Fellow of the Royal Society in 1881, and also received the honorary degree of LL.D. from the University of Dublin. He was a member of the Royal Irish Academy and of the Royal Dublin Society, and a member of the Institution of Naval Architects. He was elected a member of the Institution of Civil Engineers of Ireland in the year 1857, and for many years took an active part in its management. He contributed the following papers to its 'Transactions':—"Boyne Viaduct Experiments," 1858; "Newcastle Coal Experiments," 1859; "Effects of Salt Water on Lime Mortar," 1862; "Boyne Viaduct Girder Experiments," 1868; "Portland Cement in Marine Works," 1871; President's Address, 1872; "Strength and Properties of Riveted Joints," 1885; "The Most Economical Spans for long Girder Bridges with Numerous Spans of Equal Length," 1905.

He was Joint Honorary Secretary of the Institution of Civil Engineers of Ireland from 1862 to 1870, and was President for the years 1871 and 1872.

Dr. Stoney was elected an Associate of the Institution of Civil Engineers (London) on January 12th, 1858, and was transferred to the class of Members on November 17th, 1863. He was also a Member of the Council for a number of years. The following papers contributed by Dr. Stoney are printed in the 'Proceedings' of the Institution:—"Construction of Floating Beacons"; "Construction of Harbour and Marine Works with Artificial Blocks of Large Size"; "Description of a New Balance Bridge over the Royal Canal at Dublin."

H. G.

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FRIEDRICH WILHELM KOHLRAUSCH, 1840—1910.*

FRIEDRICH WILHELM KOHLRAUSCH was born in October, 1840, at Rinteln-on-the-Weser. His father, Rudolph Kohlrausch (1809—1858) was a distinguished physicist, who did much work of fundamental importance in clearing up the mutual relations between static electricity and galvanic electricity. He is probably best known for his determination, jointly with Wilhelm Weber, of the ratio of the electromagnetic to the electrostatic unit of electric quantity. The son studied at Erlangen and Göttingen, and took the degree of Ph.D. at Göttingen in 1863. Three years later he was appointed Professor Extraordinarius in the same University. In 1870 he went to Frankfort-on-the-Main as Professor of Physics in the Technische Hochschule, and in about a year he was appointed to a similar professorship in the Gross-Herzogliche Polytechnikum at Darmstadt. In 1875 he became Professor of Physics in the University of Wurzburg, and moved thence to the University of Strassburg in 1888. In 1895 he was appointed President of the Physikalisch-Technische Reichsanstalt at Charlottenburg, and was elected a member of the Academy of Science of Berlin, and also a Foreign Member of the Royal Society of London. He was made honorary Professor of Physics in the University of Berlin in 1900. In 1905 he resigned his post at Charlottenburg. He was elected an honorary Member of the Physical Society of London in 1906. He died at Marburg on January 17, 1910.

Kohlrausch was the author of a great number of papers giving the results of experimental investigations in many branches of physics, but the subjects which chiefly occupied him were the methods of measuring magnetic and electrical quantities. Among his contributions to this branch of science we may mention his method of determining in absolute measure the horizontal component of the earth's magnetic field and the strength of an electric current by observations of the simultaneous deflections of a tangent-galvanometer and of a suspended coil, when both instruments were traversed by the same current, the position of equilibrium of the coil when there was no current through it being such that its axis was horizontal and at right angles to the magnetic meridian.

Another important set of experiments, published in 1874, had for its object the determination of the absolute value of the "Siemens Unit" of electrical resistance. Although the result obtained was afterwards shown to be appreciably in error, this investigation was of historical importance, since it directed attention to the necessity of examining further the values

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obtained in 1863 and 1864 by Maxwell and his coadjutors for the British Association Committee on Electrical Standards.

In 1871 Kohlrausch introduced a method for measuring the electrical resistance of electrolytes, founded on the use of alternating currents, whereby the disturbing effect of the polarisation of the electrodes was almost entirely got rid of, and results were obtained of a far higher degree of accuracy than were attainable by the methods previously in use. In order that polarisation should be eliminated, it was essential that the alternations of the current should be of short period, and that the quantity of the current should be the same in each direction. In order to fulfil these conditions, Kohlrausch at first employed currents generated by the revolution of a magnet, inside a coil of wire, about a transverse axis in the median plane of the coil; in later modifications of the method the alternate currents of an induction coil were used. This investigation formed the starting point of a long and laborious series of researches by Kohlrausch himself and his pupils into the conducting power of electrolytic solutions. The examination of a great number of soluble salts in aqueous solutions of different concentrations showed that, although with dilute solutions conductivity decreases with decrease of concentration, yet the ratio of conductivity to concentration in general increases, at first nearly uniformly, but afterwards more slowly, so as to approach, in the case of each salt, a definite limit which may be called the ratio for an infinitely dilute solution. When the concentration of the solutions of different salts was expressed, not in terms of the unit mass of each salt, but in terms of its molecular mass, it was found that the ratio of concentration to conductivity was nearly the same for many allied families of salts, and that the agreement usually became closer with greater dilution. From the general results of the measurements of the conductivities of dilute solutions, Kohlrausch deduced the important conclusion that each of the ions into which an electrolytic salt may be supposed to be broken up when dissolved, moves with its own proper velocity under the influence of electromotive force, and he concluded that the conductivity of a dilute solution of a salt is simply the sum of the velocities of the anion and kation respectively under an electromotive force of one volt per centimetre. Combining this result with the ratio of the velocities, which can be deduced from Hittorf's measurements of the migration of ions, Kohlrausch deduced actual values for the mobilities of a large number of ions, and these agreed very satisfactorily with the measured conductivities of solutions of salts wherein these ions occur. This work formed the foundation of the modern electrolytic theory of solution.

Kohlrausch was one of the earliest among the teachers of physics to systematise a course of laboratory instruction for their students. His 'Leitfaden den praktischen Physik,' first published in 1870, was a most valuable help to other teachers who were in those days striving to get a general recognition by educational authorities of the fact that practical instruction in the laboratory was as essential, in the case of students of

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physics, as similar instruction had long been acknowledged to be in the case of students of chemistry. This book was translated into English by T. H. Waller and H. R. Procter soon after its first appearance, and a second English edition was published in 1883. In Germany it has gone through a great number of editions, the author continuing his careful revision and improvement to the last.

G. C. F.

SIR CHARLES TODD, K.C.M.G., 1826—1910.

CHARLES TODD died on January 29, 1910, leaving behind him more than sixty years of strenuous service to England and to South Australia. The great achievement by which he will always be remembered was his construction of the overland telegraph line from Adelaide to Port Darwin, which has been for the last forty years a main link in the chain of communication between the Australian Colonies and the old world. This was, however, but one of the many deeds he accomplished in the public service. So high a value was placed on the work which he had done for Australia that in the later years of his long life he was one of the best known and most revered men in the Commonwealth.

Todd was born at Islington on July 7, 1826, and was educated at Greenwich. In December, 1841, he entered the Greenwich Observatory as astronomical computer under Airy. In after years he often spoke of the hard work and severe discipline which Airy enforced. Yet he had a sincere liking and admiration for his stern chief, and his stories were always full of generous humour. From 1848 to 1854 he was assistant astronomer at Cambridge under Challis. In May of the latter year Airy asked him to go back to Greenwich to take charge of the new galvanic department: his work included the transmission of time signals to various parts of the country, and the dropping of time balls. In February, 1855, he was returning from a visit to Deal, where he had been readjusting the time ball apparatus at the Royal Dockyard, when he received at Tonbridge a letter from Airy, offering him, on behalf of the Colonial Office, the post of Superintendent of Telegraphs and Government Astronomer of South Australia.

With the consent of Alice Bell, of Cambridge, he accepted the offer. They were married, and left England in July, 1855, on board the "Irene," a sailing-ship of a few hundred tons. They landed at Adelaide on November 5, on which day, curiously enough, was completed the first telegraph line constructed in the province, a cheap private wire from Adelaide to Port Adelaide. After a year of small things, Todd brought

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forward his first great project, the connection of Adelaide and Melbourne by telegraph. Sailing to the latter city, he found himself the guest of the Victorian Commissioner of Trades and Customs, H. C. E. Childers, who was afterwards Chancellor of the British Exchequer. He succeeded in persuading Childers and his colleagues to take up the scheme, and rode back the 600 miles to Adelaide, mostly through the bush, alone, planning the route for the line. The work was finished in 1858, and a second and longer line from Adelaide to Sydney was completed shortly afterwards. He took advantage of the opportunities thus afforded him to make an accurate comparison of the longitudes of Adelaide, Melbourne, and Sydney, and also to find the position of the 141st meridian, which was the boundary between Victoria and South Australia. It turned out that the boundary had hitherto been placed two and a quarter miles too far west, so that Victoria was in unlawful possession of a strip of land belonging to the sister State.

His success in linking Adelaide to Melbourne and Sydney encouraged him to bring forward in 1859 the far greater scheme of the trans-continental line. It has to be remembered that most of the country to be crossed was practically unexplored; it was known only that great tracts of it were waterless desert. Northern Australia had been traversed by Gregory's expedition in 1856 from the Victoria River to the Dawson River and Moreton Bay. Todd read eagerly the history of the journey and the description of the country through which the expedition had passed, and he conceived the idea of pushing a line north from Adelaide right through the heart of the continent to emerge near the point where Gregory had entered. He could but guess at the nature of much of the interior, for Gregory had only crossed the northern portions; but the greatness of the scheme filled his mind, and he saw what its accomplishment would mean to the Australian Colonies. In that year (1859) he submitted his scheme to MacDonnell, the Governor of South Australia. In 1861–2, McDouall Stuart and his party accomplished their famous journey from south to north of the continent, actually going over most of the country through which the proposed line should run. In 1863, Todd reported that: "Whatever differences of opinion may have previously existed as to the practicability of making the vicinity of Van Diemen's Gulf the terminus of the land line, the return of Messrs. McKinlay and Stuart can leave no room for further doubt. The erection of an overland telegraph line to the north coast should be regarded as a national work, in the carrying out of which all the Colonies should unite." Men were afraid, however, of the magnitude of the task; but, in 1870, Todd's untiring advocacy at last persuaded the South Australian Government, under Strangways, to take up the scheme. The Eastern Extension Telegraph Company had offered to lay a cable from Singapore *vid* Java to Port Darwin; the several Australian Colonies were asked to help South Australia to meet the offer, but declined, so the small State had the honour of taking up the work alone. The distance to be

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covered was rather more than 2,000 miles; yet the greatness of the proposal did not lie so much in its mere magnitude as in the absolute novelties of the difficulties to be overcome. It was an immense stride from the venturesome march of a handful of explorers across the continent, to the almost contemptuous conquest of the desert by construction parties doing their work steadily day by day. The most careful plans were necessary; quantities had to be decided on a large and unusual scale, natural difficulties had to be guessed at and allowed for, and all the time the critics had to be met. Transport was, of course, one of the most serious considerations of all; as much as £130 a ton was sometimes paid. Fortunately, two of the most terrifying of possible anticipations were not realised; there was no quantity of sickness, nor was there any serious trouble from the natives. Indeed, the relations with the aborigines were rather humorous, even when irritating. Who was to foretell that the porcelain insulator could be chipped into an excellent spearhead, which could be bound to the shaft in a workmanlike manner by the aid of a little of the wire left hanging on poles by the white man? However, this fashion soon went out, hurried a little perhaps by the judicious use of the magneto machine; and the natives learnt to respect the construction which they did not understand, and even made lines of their own of sticks and string.

The contractor for the central portion of the line broke down and abandoned his undertaking. When Todd and his political chief discussed the grave situation, there was no possible decision but one; Todd must go and do the work himself. Before his vigorous attack the difficulties melted away, though not in a moment. He took the abandoned 1000-mile stretch in flank, brought the steamer "Omeo" with all his material to the mouth of the Roper River in the Gulf of Carpentaria, signed a contract with the captain as they lay outside the bar of the almost unknown river indemnifying him from the consequences of obeying orders which might lead to the loss of the ship, and triumphantly carried her eighty miles up the stream. He re-organised the transport, infused cheerfulness and enthusiasm into his men, rode every mile of the long track, surveying, planning, encouraging, until at last the work was done. Surely there have been few more striking incidents of modern enterprise than that which occurred on a cold night of August, 1872, when Todd sat down on the ground near Central Mount Stuart, with the line to the south in one hand and that to the north in the other, and joined the new countries to the old. With a little pocket instrument he spoke either way. The news spread in Adelaide and his friends came crowding to send delighted messages of congratulation. The happy man sat for hours receiving and sending, until, overcome with weariness and sleep, he begged to be allowed to say "good-night."

For thirty-eight years the trans-continental line has been part of the main channel of communication between England and Australia. A great commerce has used it freely and thriven upon it, and its effects on Australian life and progress are not to be calculated.

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The last of his great telegraphic undertakings was accomplished when he carried a line from Adelaide along the shores of the Great Bight to Eucla, on the West Australian border. Thus all the Australian States were put in touch with each other. His own State he covered with a network of means of communication, and he lived to see the telegraphic revenue mount to nearly £100,000 a year, though in the first months after his landing in South Australia it had been so small sometimes as fifteenpence in the day. In 1870 he was made Postmaster-General, and his new department also prospered. In 1906 its gross revenue was £200,000.

During this life so full of other work he did not forget his duties as Government Astronomer. The excellent little observatory in Adelaide is a testimony to his energy and his real love for astronomical science. He organised the meteorological observations of the State, and the climatic conditions of South Australia have been thoroughly well recorded and classified. With the aid of his own widely scattered offices, and his connections with the telegraphic systems of the other States, he was able to publish, and was indeed a pioneer in the publication of, weather maps. The excitement of the weather forecast was a daily incident of his life. He observed the transit of Venus in 1874, and again in 1882. On the latter occasion he took his instruments to Wentworth, on the New South Wales border. This place was in a position of strategical importance in regard to the transit, and his observations had therefore a peculiar value. He took a prominent part in the government of the public institutions of learning in the State; appeals for expert advice came to him from far beyond the limits of his own country. He spent sixty-four years in the service of the empire, fifty of them in South Australia, and the South Australian Parliament refused to pass the Bill for the compulsory retirement of septuagenarians so long as he would remain their officer.

On the completion of the overland line he received the distinction of a C.M.G., and in 1893 was advanced to a knighthood in the same order. Cambridge conferred on him the honorary degree of Master of Arts in 1886, and he became a Fellow of the Royal Society in 1889.

He had no commanding personality; at a first glance it might have been difficult to discover the source of his power. He was clearly a bright and happy man—kind, generous, full of vitality, with a perfectly boyish love of fun. Those who worked with him soon recognised his sense of proportion, his strong grasp of essentials, his acute understanding, and untiring energy. Yet, to those who knew him best, it seemed that the main secret of his success lay deeper still. It was his conviction that all those who served under him or with him were as enthusiastic as he himself for the success of the work to which they were pledged. He had no idea of using his position for his own advancement, and his natural impulse was to believe that the purpose of every man in his employ was as single as his own. As might be expected, he rarely failed to find what he thought to see. The whole of his great department was infected with his sense of duty and loyalty, his kindly

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courtesy and good humour. His remarkable capacity for organisation would in any case have created an efficient machine, but the simple goodness of his nature made his men happy in their work.

One of the most remarkable features of the public life of Australia has been the efficiency of the long series of men who have served her as heads of departments, judges, engineers, educators, geologists, astronomers, and so forth, and a very interesting account might be given of the causes which brought them forward and of the services which they rendered. Of these splendid public servants Todd was one of the best.

W. H. B.

GREVILLE WILLIAMS, 1829—1910.

CHARLES HANSON GREVILLE WILLIAMS, son of S. Hanson Williams, a solicitor, was born at Cheltenham, September 22nd, 1829. His death took place in his little cottage at Smallfields, Horley, on June 15, 1910.

His early attempts to study practical chemistry did not receive the paternal approbation; indeed, on one occasion, when the boy's pocket-money, saved up for many weeks, had been expended in the purchase of a "chemical chest," the father, with a sweep of his cane, consigned the newly-acquired treasures to destruction.

It was at the house of Dr. J. H. Gladstone, in Tavistock Square, that the writer of this notice first met Greville Williams: this was in the early fifties —probably in 1852 or 1853—when the young man was at work as a consulting and analytical chemist in Oxford Court, Cannon Street. He soon migrated to Glasgow, on being appointed first assistant to Prof. Thos. Anderson, of Glasgow University, for whom, during three years, he carried out much research work; afterwards he conducted a tutorial class under Dr. Lyon (since Lord) Playfair, at Edinburgh. During 1857 and 1858 he was lecturer on chemistry in the Normal College, Swansea. In 1858 he returned to Glasgow as chemist to the works of George Miller and Co., manufacturing chemists. Greville Williams moved to Greenford Green in 1863, remaining with Messrs. Perkin until 1868, when he entered into partnership with M. Edouard Thomas and Mr. John Dower, at the Star Chemical Works, Brentford, the firm being makers of coal-tar colours and subsisting until 1877. Mr. (now Professor) R. Meldola, F.R.S., and, after his retirement in 1872, Dr. Otto N. Witt, were in the service of this firm as chemists. It was under the auspices of Dr. Witt that some of the first azo-compounds were manufactured in this country by the firm of Williams, Thomas, and Dower. On the closing of the works Greville Williams gave up his connection with manufacturing

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chemistry and became photometric supervisor to the Gas Light and Coke Company, with whom he remained until 1901. He then retired into the country, living the life almost of a recluse, and seldom seeing his old friends and acquaintances.

At this time he had become much interested in the language of ancient Egypt, and was acquiring considerable facility in the reading and interpretation of hieroglyphic inscriptions. In this connection may be quoted a passage from a letter dated December 12, 1904, where, writing about the Sarcophagus of Seti I. in the Soane Museum, he says: "It is a real misfortune that the sarcophagus is placed where it cannot be photographed, because the old engravings of Egyptian monuments frequently exhibit mistakes in the hieroglyphic texts, but even the scribes and sculptors of the ancient dynasties were by no means impeccable in that respect, as I found when transliterating and translating the stele of Menthusa." Until rheumatism disabled him, he was an expert draughtsman and calligraphist, a fair game-shot, and an enthusiastic angler.

Although in reality a delightful companion endowed with unusual conversational powers and a keen appreciation of literary and artistic culture, Greville Williams possessed a sensitive and modest temperament which tended, especially in his later years, to isolate him from his fellows. He was, perhaps, rather more nervous about his state of health than he need have been, and in consequence, withdrew almost entirely from scientific and social intercourse. It may likewise be considered that his straitened circumstances tended in the same direction, particularly as they debarred him from continuing his researches in pure chemistry. Whenever the conditions of his daily life allowed him leisure and opportunity for original enquiry, he was an enthusiastic worker, possessed of the true chemical instinct and a general scientific aptitude, as well as a large measure of manipulative dexterity and invention. It ought to be added that Greville Williams was a most interesting correspondent, and, having a happy knack of versifying, often passed from prose into poetry in letters addressed to his more intimate friends. Two epistles of this order are at the present moment before the writer. One of these, dated March 1, 1861, deals in a playful way with the deceitfulness of unsupported spectral observations, the later epistle, written a quarter of a century afterwards (August 20, 1885), includes some humorous verses on a literary topic.

Most of Greville Williams's research work was concerned with certain groups of hydrocarbons and of volatile bases produced in the destructive distillation of organic substances, including combustible shales and coals. He made, however, a few incursions into mineral chemistry, especially in reference to peculiarities in the composition of the variety of beryl known as emerald.

Two discoveries of unusual interest were made by Greville Williams. One of these was the isolation of the most remarkable of the pentinenes, namely, isoprene ('Phil. Trans.,' vol. 150, pp. 241–255, 1860). Of this hydrocarbon

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he determined the physical constants with accuracy; it has risen in importance since its polymerisation* into caoutchouc has been achieved, and since it has been obtained from terpene. In this connection it is of interest to remember that Greville Williams ascertained that caoutchouc and terpene absorbed the same proportion of bromine. The other chief result of Williams's work was obtained in the study of quinoline bases, when he discovered cyanine or quinoline-blue ('Trans. R.S. Edin.,' vol. 31, p. 377, 1856). This body, $C_{29}H_{35}N_2I$, was the first of the quinoline dye-stuffs to be prepared. Some of these beautifully crystallised bodies have met with considerable application in photography as special sensitizers, but none of them is even tolerably fast to light.

Among the basic constituents present in certain kinds of tars from shales and coals, and in the products derived from the destructive distillation of cinchonine in the presence of potash, Greville Williams recognised and isolated several important bases. Pyridine was one of these; so also was a lutidine, perhaps a mixture of two or more of the nine possible lutidines, as well as a collidine, or a mixture of two or more of the twenty-two possible collidines; all these were found in coal tar, in Dorset shale tar, and in the distillate from cinchonine. Quinoline or leucoline, discovered by Runge, was first thoroughly investigated by Williams ('J. Chem. Soc.,' (2) 1, p. 375). Some of the members of this series of bases are of great practical importance in the synthesis of certain medicinal preparations; γ-methyl-quinoline was first obtained by Williams from cinchonine, and named lepidine (B.P., 257°): it is thought to be identical with his iridoline from coal tar. He also described, under the name of cryptidine (B.P., 274°), one of the dimethyl-quinolines—perhaps the 2·3 or the 3·4 dimethyl-quinoline of Behrend.

Much useful work was accomplished by Greville Williams in connection with the platinum compounds of the volatile bases which he examined. Some of his results were given in memoirs already named or were discussed in notes appearing in the 'Phil. Mag.' for September, 1854, and in the 'Chem. Gaz.' for August 16, and September 1 and 15, 1858. His determinations of vapour density were distinguished for the care and precision with which they were performed: these and other constants of many organic compounds were first accurately determined by him.

To about a score of memoirs and notes on organic bases which are credited to Greville Williams in the Society's Catalogue of Scientific Papers, there must be added about fifteen devoted to hydrocarbons. And during the period 1882–1885, half a dozen enquiries of a technical character, connected with coal-gas and its manufacture, were carried out and reported upon, mainly in the 'Journal of Gas Lighting.'

Greville Williams made, as before stated, a few incursions into the domain of mineral chemistry. Chief among these were his researches on beryls and emeralds which appeared in the 'Proc. Roy. Soc.' during 1873 and 1877,

* See the memoir just cited for an intimation as to such a change.

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vol. 21, pp. 409—421, and vol. 26, pp. 165—175. The earlier of these papers was devoted mainly to problems connected with the colour of the emerald but included an account of experiments on the fusion of beryl, quartz, and sapphire by means of the oxy-hydrogen blowpipe. The precautions necessary to secure clear beads of these substances were defined, while the lowering of density by their passage into the vitreous state was accurately recorded. In the second memoir the chief method in use for effecting a separation between glucina (beryllia) and alumina was critically examined and greatly improved.

Two class-books were written by Greville Williams. The more important of these was published in 1857 under the title "A Handbook of Chemical Manipulation." It contains 407 illustrations with an appendix of twenty useful tables: a supplement dealing with more recently devised apparatus and methods was brought out in 1879. The other class-book was a "Manual of Chemical Analysis for Schools," which appeared in 1858. He also wrote numerous articles for Ure's "Dictionary of Arts, Manufactures, and Mines," for Watts's "Dictionary of Chemistry," and for King's "Treatise on Coal Gas." His contributions were clear and exact, while in his accounts of materials and operations his personal experience was largely drawn upon.

In June, 1862, Greville Williams was elected to the Fellowship of the Society; he outlived the rest of the distinguished "fifteen" of that year. It was in 1862 also that he joined the Chemical Society. On November 25, 1852, he married Henrietta Bosher, who died on February 16, 1904. One son and three daughters survive.

The writer of this memorial notice has lost a friend of nearly sixty years standing—a friend of rare quality and of high Christian character.

A. H. C.

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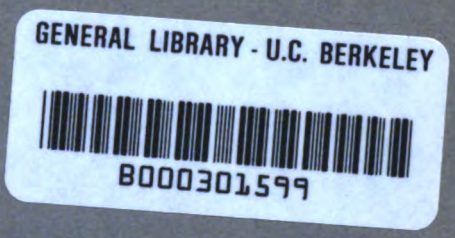

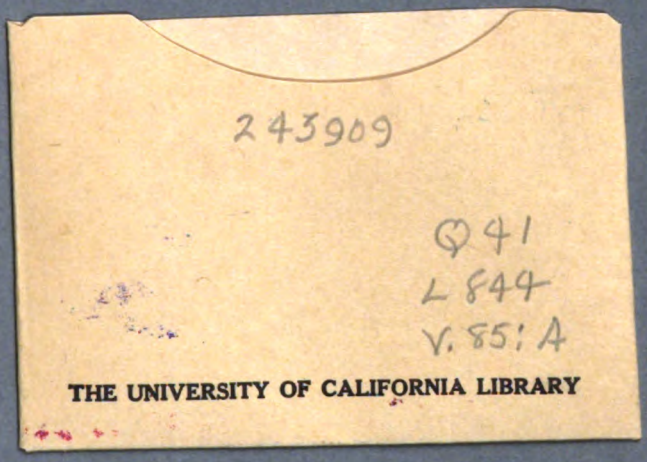

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